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ON THE OXYGEN ETHERS OF THE UREAS: METHYL- AND ETHYLISOUREA.[1]

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An investigation of the reactions of the isocarbanilides, $C_6H_5NH.C(:NC_6H_5)OR$, carried out by F. B. Dains,[2] under the direction of Professor Stieglitz,[3] in this laboratory, led to the discovery that these ethers show in some fundamentally important reactions—saponification and formation of amides—an entirely different behavior from the other known ethers with the same grouping —C(:R″)OR—, such as the ordinary acid esters RC(:O)OR and the imido ethers RC(:NH)OR. The differences appear most striking on comparison of the isocarbanilides with the last-named closely-related class of bodies, the imido ethers, the two series of compounds having the group —C(:NR)OR in common.

The hydrochlorides of the imidoethers, *e. g.*, of benzimidoether, etc., are rapidly saponified[4] in the cold in aqueous solution according to

[1] See preliminary papers by J. Stieglitz and R. H. McKee: Ber. d. chem. Ges., 32, 1494; 33, 807 and 1517.

[2] J. Am. Chem. Soc., 21, 136.

[3] This JOURNAL, 21, 101.

[4] Quantitative determinations of the velocity of saponification of imidoethers by hydrochloric acid and water were carried out by Mr. Wm. McCracken, under my direction, in 1898 and 1899. They led to the highly interesting and important result

$$(I)\quad RC(:NH)OC_2H_5 + HCl + H_2O \rightarrow RCOOC_2H_5 + NH_4Cl;$$

$$\text{or}\quad (II)\quad RC(:NH)OC_2H_5 + HCl + H_2O \rightarrow RCONH_2 + C_2H_5OH + HCl.$$

The alkyl isocarbanilides, $RNH.C(:NR)OC_2H_5$, are much more stable in dilute acid solution, and when decomposed, for instance by prolonged heating with hydrochloric acid, even in the presence of a large excess of water (1 per cent acid) they invariably give carbanilides and alkyl chlorides according to

$$C_6H_5NH(:NC_6H_5)OC_2H_5 + HCl + H_2O \rightarrow C_6H_5NHCONHC_6H_5 + ClC_2H_5 + H_2O.$$

Water apparently takes no part in the reaction.

The same contrast was shown in the behavior of the imidoethers and isourea ethers towards amines, such as anilines. Whereas imidoethers react easily, perhaps more readily than ordinary acid esters, and give amidines according to

$$RC(:NR)OC_2H_5 + C_6H_5NH_2 \rightarrow RC(:NR)NHC_6H_5 + HOC_2H_5,$$

the isocarbanilides are scarcely acted on by aniline.[1]

This striking difference in reaction of bodies of the same class of compounds toward dilute hydrochloric acid, for instance, could well be due to the change from weaker bases (the imidoethers) to much stronger ones (the urea ethers), the change producing a corresponding difference in the hydrolysis of the hydrochlorides of the bases.[2] Such a result would have an important bearing on the question of the constitution of these hydrochlorides.[3] On account of this interesting connection, it was thought advisable to take into con-

that addition of hydrochloric acid increases the velocity of saponification of an imidoether by water into ammonia and acid ester according to the above equation (I) up to a definite maximum velocity, produced by using 1 molecule of hydrochloric acid to 1 molecule of the free imidoether. Addition of more acid thereupon retards saponification (see this JOURNAL, **21**, 106). The experimental data and the discussion of the results obtained will be published later. Further work is being undertaken on the velocity of saponification of imidoethers as well as on the velocity of the action of amines on imidoethers (see below). JULIUS STIEGLITZ.

[1] Dains: *Loc. cit.*

[2] Stieglitz: This JOURNAL, **21**, 105, etc.

[3] *Ibid.*, **21**, 102.

sideration, as an alternative possibility, another force that has been recognized as playing a pronounced rôle in the saponification and amide formation of acid esters. A loss or suppression of reactivity in the formation and saponification of acid esters[1] and acid amides[2] and in the formation of imidoethers[3] has in recent years been frequently found to be due to stereochemical interference of neighboring groups. Partly, in order to test the possibility of such interference as the cause of the surprising behavior of the isocarbanilides,

$$(PhNH)C(:NPh)OR,$$

and partly for the sake of completing the study of the preparation of isourea ethers. I have undertaken, at the suggestion and under the direction of Prof. Stieglitz, to prepare and examine isoureas of simpler structure than the isocarbanilides; *viz.*, first, the oxygen ethers of monoalphyl ureas, such as

$$(C_6H_5NH)(NH:)C.OR \text{ and } (C_6H_5NCH_3)(NH:)C.OR,$$

and secondly, the oxygen ethers of urea itself,

$$NH_2C(:NH)OR.$$

The methods developed for preparing these new classes of ethers will be described in the experimental part; they have made the ethers—including notably methyl and ethyl isourea,

$$NH_2C(:NH)OCH_3 \text{ and } NH_2C(:NH)OC_2H_5,$$

as easily obtainable as any imidoether. It was found that these ethers can readily be benzoylated and condensed with phenyl isocyanate; thus were obtained isourea ethers with more negative groups, *e. g.*,

$$C_6H_5CONH.C(:NH)OR^4 \text{ and } C_6H_5CONHC(:NC_6H_5)OR,$$

[1] V. Meyer and his pupils: Ber. d. chem. Ges., **27**, 510, 1580, 3146; **28**, 182, 1254, 2773, 3197; **29**, 830, 1397.

[2] Remsen: This JOURNAL, **21**, 281, etc. Vide also, **1**, 32, 114, etc.

[3] Pinner: Ber. d. chem. Ges., **23**, 2917. [The question of interference with the saponification of imidoethers will be taken up with the velocity determinations. J. STIEGLITZ.]

[4] Dixon (J. Chem. Soc. (London), 1899, 380) obtained the same substance by treating benzimidothiocarbonic esters, $C_6H_5CON:C(SR)OR$, with ammonia.

Vide also Wheeler and Johnson, this JOURNAL, **24**, 189. The experiments described by me were all completed by last May (1900) before the appearance of Dr.

etc. Every isourea ether obtained gave an alkyl chloride and a urea on heating with even very dilute hydrochloric acid, *e. g.*, according to

$$NH_2C(:NH)OCH_3 + HCl + H_2O \rightarrow NH_2CONH_2 + ClCH_3 + H_2O.$$

The study of the behavior of the new urea ethers towards amines has not been completed, but the question has been thoroughly investigated in the case of the monophenylated isoureas. In no instance was a smooth formation of an amide (guanidine)[1] observed, according to

$$C_6H_5NHC(:NH)OC_2H_5 + C_6H_5NH_2 \rightarrow (C_6H_5NH)_2C:NH + C_2H_5OH.$$

The simple isourea ethers show, therefore, the same characteristic lack of power to form normal saponification-products and amides as the isocarbanilides; their characteristic behavior is, therefore, certainly not due to stereochemical interference of the groups attached to the nitrogen atoms and must, as was expected, be due to other causes.[2]

EXPERIMENTAL PART.

I. The Oxygen Ethers of the Monoalphylureas.

The oxygen ethers of the diphenylureas are prepared from the carbodiimides by the addition of alcohol according to

$$C_6H_5N:C:NC_6H_5 + HOR \rightarrow (C_6H_5NH)C(:NC_6H_5)OR.$$

Wheeler's interesting paper (September number of this JOURNAL). Dr. Wheeler describes two or three of the bodies mentioned in the text, such as the ethyl and methyl benzoylphenylisoureas, which were obtained in approximately pure condition by means of Dixon's method. Dr. Wheeler also calls attention to the characteristic tendency of the isoures ethers to give alkyl chlorides with aqueous hydrochloric acid (Stieglitz: *Loc. cit.*; Dains: *Loc. cit.*; Stieglitz and McKee: Ber. d. chem. Ges., 33,1517), the acylated or more negative ones even reacting in that direction in the cold. In the case of one of these the solid hydrochloride was isolated by me and found to decompose spontaneously in the desiccator with evolution of alkyl chloride (p. 233). This behavior, it may be added, is entirely analogous to the behavior of the more negative imidoethers towards hydrogen chloride (*e. g.*, Stieglitz and Lengfeld: this JOURNAL, 16, 75; 17, 98; Ransom: *Ibid.*, 23, 46).

[1] The actual reaction-products were interesting and will be described in the experimental part.

[2] The application of the results obtained to the theories suggested in this JOURNAL, 21, 101, will be discussed by Prof. Stieglitz in a later paper after the collection of more data.

This addition may be accomplished by heating the diimide with absolute alcohol to 160° to 180° in sealed tubes,[1] or more simply in the cold by the action of sodium alcoholate[2] in alcohol solution on the carbodiimide, the reaction proceeding with great vigor and smoothness in the latter case.[3]

For the preparation of the monophenylisourea ethers the addition of alcohol to phenylcyanamide, $C_6H_5NH.CN$ (I), or possibly $C_6H_5N : C : NH$ (II)[4], was attempted on the lines mentioned; although in other addition reactions, *e. g.*, with hydrogen sulphide,[5] aniline,[6] etc., no great differences between the phenylcyanamides and the carbodiimides seem to have been noted,[7] it was found impossible to add alcohol to phenylcyanamide by the methods which had proved so successful with the carbodiimides. As such a behavior might be due to the presence of a nitril group in phenylcyanamide according to constitution (I), the compound was treated with alcohol (1 mol.) and hydrogen chloride (1 mol.) according to Pinner's method for converting a nitril into an imidoether. Only traces of a substance were obtained, which gave ethyl chloride when heated in a current of dry hydrogen chloride gas, in the way that imidoethers and isourea ethers do. However, it was soon found that by modifying the method and using a very large excess of alcohol, phenylcyanamide can be converted quantitatively into monophenylisourea ethers according to

$$C_6H_5NHCN + HOC_2H_5 + HCl \rightarrow C_6H_5NHC(:NH)OC_2H_5.HCl.$$

In this way methyl phenylisourea, ethyl phenylisourea, and ethyl-*o*-tolylisourea were prepared with ease in quantity.

The fact, on the one hand, that sodium alcoholate is taken

[1] Lengfeld and Stieglitz: Ber. d. chem. Ges., **27**, 926.

[2] Stieglitz: *Ibid.*, **28**, 573.

[3] A third method (Lengfeld and Stieglitz: This JOURNAL, **17**, 112), which consists in treating the diimide successively with dry hydrogen chloride and sodium alcoholate, is probably identical in the final character of the reaction with the second method given above.

[4] Meyer and Jacobson: Vol. II, 197.

[5] Weith: Ber. d. chem. Ges., **7**, 1303; **9**, 819.

[6] Weith: *Ibid.*, **7**, 13; Cahours and Cloez: Ann. Chem. (Liebig), **90**, 93.

[7] We now have reason to suspect that carbodiphenylimide is really the more reactive of the two.

up by carbodiphenylimide with great violence,[1] but not at all by phenylcyanamide, and the resemblance, on the other hand, in the method of adding alcohol to nitrils and to phenylcyanamide seemed strongly to favor, incidentally, the nitril constitution for phenylcyanamide, $C_6H_5NH.C:N$, as against the carbodiimide constitution, $C_6H_5N:C:NH$.[2] How little such synthetic methods can be relied upon for distinguishing between tautomeric formulæ, without exhaustive study, is shown by the interesting fact that alkylphenylcyanamides,

$$(RNC_6H_5).C:N,$$

undoubted nitrils, were found to take up alcohol far more readily by means of sodium alcoholate than by treatment with alcohol and hydrogen chloride, addition in the latter case taking place much more slowly than with phenylcyanamide. Undoubted carbodiimides, therefore, *e. g.*, $C_6H_5N=C=NC_6H_5$, and unquestionable nitrils, *e. g.*, $C_6H_5NCH_3.C:N$, resemble each other in taking up alcohol to form isourea ethers easily in the presence of sodium alcoholate—while phenylcyanamide, whose constitution must resemble one or the other, does not take up alcohol at all under these conditions, but does so in acid solution more rapidly than the others. The chief regularity observed in this question is that those compounds which form metal salts, such as phenylcyanamide, of which salts $M'(C_6H_5NCN)$ are known, and cyanamide, which gives salts, $M'_2(N_2C)$, are less readily acted on by sodium alcoholate and more easily by hydrochloric acid and alcohol. With fully substituted cyanamides and carbodiimides which do not form metallic salts, but do absorb hydrochloric acid easily, the conditions are reversed. The conclusion is inevitable that constitution plays no rôle in this reaction while electric conditions of the molecule do.

Ethyl Phenylisourea (*Ethyl Phenylimidocarbamate*), $NH_2.C(:NC_6H_5)OC_2H_5$ or $NH:C(NHC_6H_5)OC_2H_5$.[3]—The

[1] Stieglitz: *Loc. cit.*

[2] See preliminary reports, *Loc. cit.*

[3] The two formulæ represent the two tautomeric constitutions for the urea ether. As in the case of other amidines (Von Pechmann: Ber. d. chem. Ges., **28**, 2362 and 869; **30**, 1779. Wheeler: This JOURNAL, **19**, 367; **20**, 481 and 853; Marckwald: Ann. Chem. (Liebig), **286**, 348) only one form appears to be stable. The determination of

addition of alcohol to phenylcyanamide was first attempted, as explained above, by the methods which had proved successful with the carbodiimides. As the negative result of the experiment is of some interest, the conditions observed will be very briefly given.

An alcoholic solution of crystallized phenylcyanamide,[1] $C_6H_5NH.CN + \frac{1}{2}H_2O$, was added to a cold solution of sodium ethylate, prepared by dissolving slightly more than one equivalent of sodium in absolute alcohol, and the whole was allowed to stand a day and a half. On pouring the mixture into water and neutralizing with acetic acid, the phenylcyanamide was recovered unchanged. Heating the mixture on the water-bath gave no better result.

Equivalent amounts of crystallized phenylcyanamide and absolute alcohol were heated in a sealed tube to 180°–200° for three and a half hours. On treating the contents of the tube with water no basic oil separated, thus showing that the phenylisourea ether had not been formed.

The method of preparation finally used was as follows: Three to 3.6 grams (1.5 to 2 mol.) dry hydrogen chloride were passed into a well cooled solution of 6.3 grams (1 mol.) crystallized phenylcyanamide in 18 to 23 grams (8 to 10 mol.) absolute ethyl alcohol. After standing two days the mixture was slowly poured into an excess of a cold 15 per cent solution of potassium hydroxide. The oil separating was taken up with ether and the extract washed several times with small amounts of water and dried with anhydrous sodium sulphate. After filtering from the sodium sulphate, by means of a siphon filter, the ether was distilled off on the water-bath and the oil remaining fractioned *in vacuo*. The second distillation gave fractions boiling at 138° to 138°.5, 138°.5, and 138°.5 to 139°.5 at 18 mm. pressure, the middle fraction being three-fourths of the entire amount. The yield of pure oil was 77.5 per cent of the theory.

the actual constitution by distinguishing between the two forms was not attempted, because the methods used in the case of other amidines did not seem at all conclusive. To avoid needless occupation of space only one formula will be used hereafter in such cases, it being understood that the tautomeric form is considered equally justified.

[1] Hofmann: Ber. d. chem. Ges., 18, 3220.

Ethyl phenylisourea is a colorless liquid having a basic amine-like odor. It is readily soluble in all the ordinary organic solvents, and slightly soluble in water, the solution resulting being strongly alkaline.

The ether boils at the following temperatures:

	Temperature.
12 mm.	131°
18 mm.	138°.5
32 mm.	155°

It could not be solidified by cooling to —15°. The index of refraction as determined with an Abbé refractometer is 1.5575 at 23°. Analysis:

I. 0.1642 gram substance gave 0.3971 gram CO_2 and 0.1152 gram H_2O.

II. 0.2861 gram substance gave 0.6913 gram CO_2 and 0.1937 gram H_2O.

	Calculated for $C_9H_{12}N_2O$.	Found. I.	Found. II.
C	65.77	65.96	65.90
H	7.38	7.86	7.59

Dry hydrogen chloride was passed over a little of the oil contained in a test-tube connected with an azotometer. The hydrogen chloride was at first absorbed; on heating the tube in the water-bath to about 78° decomposition occurred, a gas (ethyl chloride) being evolved, which was not absorbed by a solution of caustic potash and which burned with a green flame. The solid in the tube, after crystallization from hot water, melted at 145°, and mixed with synthetic monophenylurea[1] (melting-point 147°) it melted half a degree higher. The decomposition takes place, therefore, according to

$$C_6H_5NHC(:NH)OC_2H_5 + HCl \rightarrow C_2H_5Cl + C_6H_5NHCONH_2,$$

confirming the constitution given to the isourea ether.

Ethyl Phenylisourea Hydrochloride, $C_6H_5NHC(:NH)OC_2H_5.HCl$.—A solution of ethyl phenylisourea in absolute ether, treated with dry hydrogen chloride, gave an immediate white crystalline precipitate of the hydro-

[1] Weith: Ber. d. chem. Ges., 9, 820.

chloride. This was rapidly filtered off, well washed with absolute ether, and dried on a clay plate *in vacuo* over solid caustic potash and sulphuric acid. It was afterward finely powdered and replaced in the vacuum desiccator.

0.2883 gram substance required 14.35 cc. tenth-normal $AgNO_3$ (using chromate as an indicator).

	Calculated for $C_9H_{13}N_2OCl$.	Found.
Cl	17.67	17.65

The analysis shows that, while the phenylisourea contains both an anilide and an imide group, yet it is a monacid base towards hydrochloric acid, as far as the formation of a stable salt is concerned. The same result was obtained (see below) with hydrochlorplatinic acid. The water solution of the hydrochloride does not change the tint of neutral litmus paper, the solution being *exactly neutral* so far as could be determined by the use of litmus and of methyl orange as indicators.

If the ether solution is saturated with hydrogen chloride, a salt is obtained whose solution in water is acid to litmus and which contains a higher percentage of chlorine. One sample made contained 18.73 per cent, but on standing in the desiccator several days the percentage of chlorine became less, although it did not become quite as low as that of the pure monohydrochloride.

Ethyl phenylisourea hydrochloride is a white crystalline solid soluble in water, methyl and ethyl alcohols, chloroform, and acetone; insoluble in benzene, ligroin, and ether. Heated in a melting-point tube the salt melts at 110° with evolution of ethyl chloride. Once having been freed from excess of hydrogen chloride the salt is quite stable, seemingly being entirely unaffected by exposure to the air. Its stability towards water was shown by the fact that it could be crystallized from its concentrated water solution, forming beautiful clusters of needles an inch in length radiating from a common center.

Chlorplatinate of Ethyl Phenylisourea, $(C_9H_{12}N_2O)_2,H_2PtCl_6$. —On mixing somewhat concentrated absolute alcohol solutions of ethyl phenylisourea and chlorplatinic acid, the chlorplatinate slowly separated in the form of dark-yellow plates.

It was filtered off, washed with absolute ether, and dried on a clay plate *in vacuo* over sulphuric acid. It melts with decomposition at 160°, is insoluble in water, and difficultly soluble in alcohol.

Analysis:

0.1392 gram substance gave 0.0369 gram platinum.

	Calculated for $C_{18}H_{28}N_4O_2PtCl_6$.	Found.
Pt	26.40	26.51

Action of Air and Water on Ethyl Phenylisourea.

Imidoethers,[1] on exposure to the air or in contact with water, slowly give an acid amide and alcohol according to

$$RC(:NH)OR' + H_2O \rightarrow RCONH_2 + R'OH.$$

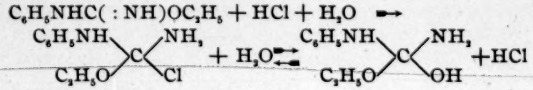
Under similar treatment the isourea ethers are very stable. Ethyl phenylisourea exposed to the air apparently undergoes no change. Neither did contact with water for six months nor heating with water for six hours at 100° produce a perceptible change. However, when the time of heating with water in a sealed tube was lengthened to fifteen hours there was some separation of monophenylurea. No ammonia or aniline could be found, making it certain that no urethane had been formed.

Dains[2] found that water does not act on ethyl diphenylisourea at ordinary temperatures.

Action of Dilute Hydrochloric Acid on Ethyl Phenylisourea.

The interest attaching to the products of the action of dilute hydrochloric acid on isourea ethers is explained in the introduction. If hydrolysis or saponification occurs as in the case of the imidoethers, ethyl phenylisourea would react as follows:[3]

I. $C_6H_5NHC(:NH)OC_2H_5 + HCl + H_2O \rightarrow$



[1] Wheeler: This JOURNAL, 17, 398.
[2] J. Am. Chem. Soc., 21, 166.
[3] Stieglitz: *Loc. cit.*; Dains: *Loc. cit.*

and would give either ammonia (or aniline) and a urethane or alcohol and phenylurea according to

a. $NH_3 + C_6H_5NHCOOC_2H_5$;
or *b*. $C_6H_5NH_2 + NH_2COOC_2H_5$;
or *c*. $C_2H_5OH + C_6H_5NHCONH_2$.

On the other hand it could give, without hydrolysis, as in the case of the isocarbanilides, ethyl chloride and phenylurea according to

II. $C_6H_5NH-C(NH_2)(Cl)(OC_2H_5) \rightarrow C_6H_5NHCONH_2 + ClC_2H_5$.

The following experiments show that ethyl phenylisourea is uncommonly stable towards aqueous hydrochloric acid at ordinary temperatures and is decomposed by it at 100° according to II and not according to I—in a word, as was expected, without hydrolysis of the urea ether salt.

Ethyl phenylisourea (1 mol.) with 8 per cent hydrochloric acid (1.1 mol.) was heated to boiling for two minutes, cooled, and kept at the room temperature. After two months the solution was still perfectly clear and a drop of alkali precipitated the unchanged urea ether.

No change could be detected after heating the urea ether at 50°, for three and a half hours, with normal hydrochloric acid.

A solution of 1.7 grams ethyl phenylisourea in slightly more than 1 molecule 8 per cent hydrochloric acid was heated four and a half hours in a sealed tube in a Victor Meyer water-bath. The tube opened with considerable pressure, due to ethyl chloride, as the gas burned with the characteristic green flame. A deposit of crystals was separated from the mother-liquor (*a*) and then, to test them for any admixture of phenylurethane, distilled with steam, but no trace of the urethane could be found in the distillate. A single recrystallization of the residue gave pure monophenylurea. The clear filtrate (*a*) gave, with sodium hydroxide, an emulsion which was extracted with ether. Careful evaporation of the

ether left a few drops of an oil, which was shown to contain a little aniline by the bleaching-powder test and unchanged isourea ether by the formation of ethyl chloride when heated in a current of dry hydrogen chloride. That the small amount of aniline found was most likely due to saponification of some of the phenylurea by the dilute acid was proved by heating monophenylurea (1 mol.) with dilute acid ($\frac{3}{4}$ mol.) for two hours, and showing the presence of aniline in the filtrate in approximately the same amount as found before.

The chief products of the action of hydrochloric acid on ethyl phenylisourea are, therefore, ethyl chloride and phenyl urea according to equation II.

Action of Ammonia on Ethyl Phenylisourea.

In the introduction attention was called to the striking contrast in the behavior of isocarbanilide ethers and imidoethers towards amines. Thus ammonia readily reacts with benzimido ether with formation of benzamidine and alcohol[1] according to

$$C_6H_5C(:NH)OC_2H_5 + NH_3 \rightarrow C_6H_5C(NH_2)(NH_2)(OC_2H_5) \rightarrow C_6H_5C(NH_2)=NH + C_2H_5OH.$$

If a similar action occurred with the isourea ethers, ethyl phenylisourea should give monophenylguanidine and alcohol according to

$$C_6H_5NHC(:NH)OC_2H_5 + NH_3 \rightarrow C_6H_5NH-C(NH_2)(NH_2)(OC_2H_5) \rightarrow C_6H_5NH-C(NH_2)=NH + C_2H_5OH.$$

The experiments show that no action of this nature occurs, the urea ether being entirely unaffected by ammonia.

[1] Stieglitz: *Loc. cit.*

Ethyl phenylisourea, after having been in contact with concentrated aqueous ammonia for two months at the room temperature, was recovered unchanged.

No action could be detected after heating the urea ether in a sealed tube with alcoholic ammonia for three hours at 140°, the urea ether being again entirely recovered.

If ammonia reacted with ethyl phenylisourea according to the above equation, monophenylguanidine would be one of the products. Feuerlein[1] has described a substance as monophenylguanidine, but the properties given are not those one would expect a guanidine to have.[2] For fear from lack of exact knowledge concerning its properties of overlooking the base if it had been formed only in small quantity, it seemed best to prepare the guanidine synthetically. Even after becoming familiar with its properties none could be found when phenylisourea was treated with ammonia.

Monophenylguanidine, $C_6H_5NHC(:NH)NH_2$.—Equivalent amounts of cyanamide and aniline hydrochloride were placed in a sealed tube with double the weight of absolute alcohol and heated at 100° for two and a half hours. The tube opened with no pressure. Its contents were evaporated on the water-bath nearly to dryness and redissolved in a little water. Addition of a concentrated solution of potassium hydroxide caused the guanidine to separate as an oil, which soon solidified and was then filtered off. The yield was excellent.

Monophenylguanidine is soluble in water, alcohol, ether, warm chloroform, and warm benzene. Crystallized from the last solvent it melted at about 66°.[3] It decomposes on attempting to distil it *in vacuo*. The free base is hygroscopic and takes up carbon dioxide; for identification the chlorplatinate and benzoyl derivatives were prepared and analyzed.

Monophenylguanidine Chlorplatinate,[4] $(C_7H_9N_3)_2H_2PtCl_6$.—Alcoholic solutions of monophenylguanidine and chlorplatinic

[1] Ber. d. chem. Ges., 12, 1602.

[2] Judging from the properties Feuerlein gives, the body he had was possibly the ammonium salt of phenylcyanamide.

[3] Feuerlein could not have had monophenylguanidine, for he describes the body as exploding when heated.

[4] Feuerlein states that monophenylguanidine does not form a chlorplatinate.

acid were mixed, the resulting precipitate filtered off, washed with a little alcohol and ether, and dried *in vacuo*. The chlorplatinate is soluble in water and warm alcohol; it melts with decomposition at 197° to 198°.

0.2693 gram substance gave 0.0774 gram platinum.

0.1256 gram substance gave 13.9 cc. moist nitrogen at 19° and 745.8 mm.

	Calculated for $C_{14}H_{20}N_6PtCl_6$.	Found.
Pt	28.65	28.74
N	12.39	12.53

Dibenzoylphenylguanidine, $C_6H_5CONH.C(:NCOC_6H_5).NHC_6H_5$. — When monophenylguanidine was treated with the equivalent amount of benzoyl chloride there was formed a small amount of a solid which proved to be not the mono- but the dibenzoyl derivative. This dibenzoyl derivative was formed quantitatively when monophenylguanidine (1 mol.) was dissolved in dilute caustic potash, benzoyl chloride (2 mol.) added, and the whole shaken until all odor of the acid chloride had disappeared. The resulting solid, when recrystallized from boiling alcohol, in which it was only slightly soluble, gave needles melting at 183°.5.

I. 0.1945 gram substance gave 0.5206 gram CO_2 and 0.0903 gram H_2O.

II. 0.1630 gram substance gave 18 cc. moist nitrogen at 24° and 745.4 mm.

	Calculated for $C_{21}H_{17}N_3O_3$.	Found. I.	Found. II.
C	73.41	73.00	....
H	5.00	5.20	....
N	12.27	....	12.21

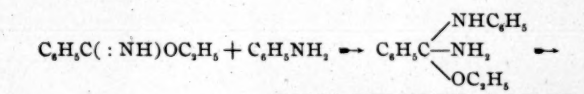
While the free monophenylguanidine has hitherto been unknown the chloraurate[1] and picrate[2] have been described. Emick describes the gold salt as forming yellow-brown needles soluble in hot water. I found the needles to be of a light-yellow color after recrystallization from hot water. Prelinger

[1] Emick: Monatsh. Chem., 12, 17.
[2] Prelinger: *Ibid.*, 13, 100.

describes the picrate obtained from Emick's chloraurate as forming dark-yellow needles melting at 208° to 214.° I found the needles to melt at 221°.

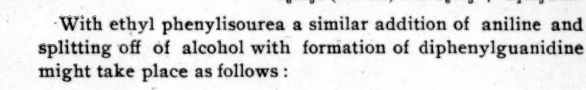
Action of Aniline on Ethyl Phenylisourea.

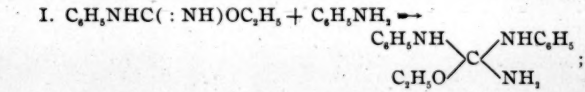
Imidoethers react smoothly with aniline, presumably first forming an addition-product from which, by the loss of alcohol, amidines result.



$$C_6H_5C(:NH)NHC_6H_5 + C_2H_5OH.$$

With ethyl phenylisourea a similar addition of aniline and splitting off of alcohol with formation of diphenylguanidine might take place as follows:

I. 

IIa. 

$$C_6H_5NHC(:NH)NHC_6H_5 + C_2H_5OH.$$

Experiment showed, however, that *no* guanidine results from the action of aniline on ethyl phenylisourea. This result is the more surprising as the actual products of the reaction point to the formation of the very reaction-product I. which, it would be supposed, would easily yield the guanidine. The most prominent reaction-products proved to be monoethylaniline and ethylamine, monophenylurea and diphenylurea. The formation of these four substances may be simply explained by assuming them to be decomposition-products of the addition-product I.:

$$\text{II}b.\ C_6H_5NHC_2H_5 + C_6H_5NHCONH_2;$$

$$\text{II}c.\ C_2H_5NH_2 + C_6H_5NHCONHC_6H_5.$$

But if that is the case, the absence of any tendency to form

the guanidines is most surprising. In point of fact, the power of the urea ether to *alkylate* amines is worthy of note. No evidence of the occurrence of the fourth possible reaction,

$$\text{II}d.\ NH_3 + C_6H_5NHC(:NC_6H_5)OC_2H_5,$$

the formation of ammonia and ethyl isocarbanilide could be detected. The following is the experimental work on which the above statements are based:

Aniline and ethyl phenylisourea were heated for several hours at 150° without reacting. When molecular proportions of aniline and the phenylisourea were heated together for four hours at 175° a partial reaction occurred.

The tube opened with slight pressure, due to ethylamine, as was shown by passing the gas into dilute hydrochloric acid. On treating the residue left on evaporating the acid solution with chloroform and caustic potash, a strong isonitril odor was obtained. The contents of the tube were treated with cold dilute hydrochloric acid, filtered from a small amount of tar, and the filtrate (A) brought to boiling, but no precipitate separated, showing the absence of any ethyl isocarbanilide, which, if present, would have given a precipitate of carbanilide.[1] The tar, when extracted with boiling water, gave crystals of monophenylurea, identified by the melting-point (when mixed with the synthetic monophenylurea the melting-point was unchanged). The tarry mass which had been extracted with hot water was dissolved in hot alcohol, but the product which separated on cooling, while probably carbanilide, could not be positively identified owing to its small amount and to the simultaneous separation of the tar. In another experiment,[2] where the experiments were but slightly changed, carbanilide was completely identified. The dilute acid solution (A) was made alkaline and distilled with steam; in the distillate, besides much aniline (bleaching-powder test), the presence of ethylaniline and ethylphenylisourea was shown as follows: Ethylaniline was identified by acidifying a portion of the distillate, adding a little sodium nitrite and obtaining the yellow solution of nitrosoethylaniline. For confirmation,

[1] Lengfeld and Stieglitz: *Loc. cit.*

[2] Page 225.

parallel experiments were carried out with a solution of aniline and the isourea ether, and with a solution of aniline, isourea ether, and a little ethylaniline; only the latter gave the yellow-colored solution expected. That unchanged ethyl phenylisourea was present was made certain by heating a few drops of the oil from the distillate in a current of hydrogen chloride and obtaining ethyl chloride. The residue left in the flask, after distilling with steam, was made acid, evaporated to a small volume, filtered, and the filtrate made alkaline with potassium hydroxide, but no guanidine separated.

If the interpretation that has been given of the action of aniline on ethylphenylisourea is correct, the presence of a small amount of acid would accelerate the reaction, serving as it would to bring the double bond between the carbon and nitrogen atoms into the nascent condition,[1] and conversely a large excess of acid would retard, if not entirely stop, the reaction. Experiments fully confirmed these conclusions.

Molecular proportions of phenylisourea and aniline, with 1 molecule of hydrochloric acid, reacted at 50° in three hours, giving ethylaniline, ethylamine, monophenylurea, and carbanilide.

When aniline and ethyl phenylisourea were heated under the same conditions, excepting that four times as much acid was present, no action took place.

Action of Benzoyl Chloride on Ethyl Phenylisourea.

Dains[2] found that acyl chlorides acted upon ethyl isocarbanilide with the formation of ethyl chloride and a trisubstituted urea according to

$$C_6H_5NHC(:NC_6H_5)OC_2H_5 + R.COCl \rightarrow C_6H_5NH.CO.N(.COR)C_6H_5 + C_2H_5Cl.$$

This action of acyl chlorides corresponds in every way to that

[1] If the constitution of the urea ether salts is $(RNH)(NH_2)CCl(OR)$, the presence of insufficient acid to neutralize all of the base would tend to make the molecules change continually from the saturated salt condition to the unsaturated base $RNHC(:NH)OR$ and back again. Excess of acid would form the stable saturated salt. (Vide Stieglitz: "On the Constitution of the Salts of Carbimido Derivatives," *Loc. cit.*, p. 109).

[2] J. Am. Chem. Soc., **21**, 181.

found by Wheeler and Walden[1] to occur when imidoesters having no hydrogen directly bound to the nitrogen atom are acted upon by acyl chlorides.

I found that the monophenylated urea ethers can be benzoylated quite readily without the loss of the alkyl group, the reaction proceeding along the same lines as with the imidoethers, which have a replaceable hydrogen atom in the imido group. The benzoyl compounds in the urea series are much more stable towards moisture, ammonia, aniline, etc., than the benzoyl imidoethers. Towards heat the stability is reversed, it being found impossible to distil the benzoylated urea ethers without decomposition,[2] a property which rendered their purification difficult. This difficulty was in good part overcome by taking every care in the preparation to obtain a pure compound. A compound such as ethyl phenylisourea could produce two isomeric benzoyl derivatives, *viz.*,

$$C_6H_5NH.C(:NCOC_6H_5)OC_2H_5$$

and

$$C_6H_5CO(C_6H_5)N.C(:NH)OC_2H_5.$$

As a matter of fact, a mixture of the two benzoyl derivatives is formed, for, when the resulting product is heated with hydrochloric acid a small amount of benzanilide, having the phenyl and benzoyl groups linked to the same nitrogen atom, is found as well as a larger amount of symmetrical benzoylphenylurea, in which the groups are bound to different nitrogen atoms. In the case of the benzoylated ethyl ether of phenylisourea it has not been found possible as yet to separate the isomers, but the separation was accomplished in the corresponding methyl series, and the compounds in question will be described more completely below. Working in the cold, the chief product is the symmetrical ether,

$$C_6H_5NH.C(:NCOC_6H_5)OC_2H_5.$$

Ethyl phenylisourea (2 mol.) was dissolved in five times the volume of absolute ether, and to this solution, kept in a freezing-mixture, there was slowly added, by means of a

[1] This JOURNAL, 19, 130.

[2] This has since been confirmed by Wheeler's experience. See this JOURNAL, 24, 219.

dropping funnel, a solution of benzoyl chloride (1.05 mol.) in four times the volume of absolute ether. In order to complete the reaction, the corked flask was allowed to stand an hour and a half in the freezing-mixture, and then, after reaching the room temperature, the ether solution was filtered by means of a siphon filter, from the solid precipitate of ethyl phenylisourea hydrochloride. Evaporation of the ether filtrate in a vacuum desiccator over sulphuric acid and caustic potash gave an oil mixed with a little solid. The former was taken up with ligroin (boiling-point 40° to 60°) and filtered from the undissolved solid, which consisted principally of the hydrochloride of ethyl phenylisourea. Sometimes there was formed at this point a small amount of a solid slightly soluble in ligroin and insoluble in water, the mass of which was greater if the operation was hurried and the temperature not kept low. The ligroin solution, on evaporation *in vacuo* over sulphuric acid, caustic potash, and paraffin, left the ethyl phenylbenzoylisourea as a nearly clear oil. On attempting to distil the oil at a pressure of 9 mm. it decomposed when the metal-bath reached 200°; on opening the flask the strong odor of phenyl isocyanate was present, and after that had disappeared an odor like that of benzonitril remained. The uninviting tar remaining in the flask was not investigated.

An analysis of the carefully prepared oil was made without distillation or farther purification and gave the following figures:

0.1401 gram substance gave 13.0 cc. moist nitrogen at 24° and 754.8 mm. pressure.

	Calculated for $C_{18}H_{18}N_2O_3$.	Found.
N	10.47	10.39

The product is therefore nearly pure ethyl benzoylphenylisourea. The oil consists chiefly of the symmetrical compound ethyl phenylimidobenzoylcarbamate,[1]

$$C_6H_5CO.N : C(NHC_6H_5)OC_2H_5,$$

with the benzoyl group attached to the non-phenylated ammonia rest. This is shown by the fact that treatment with

[1] See Wheeler: This JOURNAL, 24, 219.

dry hydrogen chloride decomposes it into ethyl chloride and symmetrical benzoylphenylurea, $C_6H_5CONHCONHC_6H_5$, (melting-point 203°.5 to 204°, not changed by mixing with the synthetically[1] prepared compound). At the same time the benzoylated urea ether probably contains a small amount of the isomeric compound with the benzoyl group attached to the aniline radical, ethyl imidobenzoylphenylcarbamate,

$$C_6H_5CO(NC_6H_5)C(:NH)OC_2H_5.$$

After standing for some months in a desiccator the oil deposited a quantity of slender prisms, which resembled in habit the corresponding solid asymmetric benzoyl derivative of methyl phenylisourea (see below). The difference in solubility of the oil and solid in low-boiling ligroin did not admit of their separation as in the methyl series.

Action of Dilute Hydrochloric Acid on Ethyl Benzoylphenylisourea.

The oily mixture of the two isomeric ethyl benzoylphenylisoureas was heated for three and a half hours at 100° with slightly more than the equivalent amount of normal hydrochloric acid. The tube opened with pressure due to ethyl chloride, which burned with its characteristic green-tinged flame. The solid was filtered off and by fractional crystallization from alcohol separated into benzoylphenylurea (melting-point 203°, unchanged when mixed with the synthetic product[2]) and about a fourth as much benzanilide (melting-point 160° to 161°, unchanged when mixed with the synthetic product). From the relative amounts of the solids obtained one can roughly estimate the percentage of each isomer in the mixture.

No alcohol could be found in the filtrate by the iodoform test.

Methyl Phenylisourea (*Methyl Phenylimidocarbamate*), $NH:C(NHC_6H_5)OCH_3$, was prepared by treating 16 grams (1 mol.) of crystallized phenylcyanamide dissolved in 40 grams (10 mol.) of absolute methyl alcohol with 7.6 grams

[1] Kuhn: Ber. d. chem. Ges., 17, 2881.
[2] *Loc. cit.*

(1⅔ mol.) of dry hydrogen chloride. After standing two days the solution was worked up by the same method that was used in the case of the ethyl ether.

Methyl phenylisourea boils at the following temperatures:

	Temperature.
10 mm.	124°
15 mm.	133°
23 mm.	140°

It solidifies readily, forming a beautiful crystalline body (melting-point 46°.5) having a basic fishy odor and a bitter taste. The yield varied between 75 and 85 per cent of the theory. A freshly distilled portion was used for analysis:

I. 0.2742 gram substance gave 0.6437 gram CO_2 (H_2O lost).

II. 0.1470 gram substance gave 24.6 cc. moist nitrogen at 21° and 744.6 mm.

	Calculated for $C_6H_5NHC(:NH)OCH_3$.	Found. I.	II.
C	63.92	64.02	....
H	6.73	lost	....
N	18.70	....	18.75

Methyl Phenylisourea Hydrochloride, $C_6H_5NHC(:NH)OCH_3.HCl$, was formed by treating the solution of the methyl compound in absolute ether with hydrogen chloride. Like the hydrochloride of the ethyl ether this body, unless filtered and washed rapidly, takes up moisture from the air, forming a smear. When once freed from the excess of hydrogen chloride and ether, however, it is stable in the air. The hydrochloride is soluble in water and the ordinary organic solvents except ether, ligroin, and benzene. Heated in a tube it melted at 90° with evolution of a gas, which burned at the mouth of the tube with a green flame, showing it to be methyl chloride. The tube and contents were allowed to cool, and on reheating the substance melted at 145° (pure monophenylurea melts at 147°). The following action occurs:

$$C_6H_5NHC(:NH)OCH_3.HCl \rightarrow CH_3Cl + C_6H_5NHCONH_2.$$

The aqueous solution of the hydrochloride is neutral to litmus.

0.1305 gram substance required 6.97 cc. tenth-normal $AgNO_3$ (chromate indicator).

	Calculated for $C_8H_{11}N_2OCl$.	Found.
Cl	18.99	18.93

Methyl Phenylisourea Sulphate, $(C_8H_{11}N_2O)_2SO_4$.—A weighed amount of the crystals of the free base was dissolved in the theoretical volume of normal sulphuric acid and the resulting neutral solution allowed to evaporate *in vacuo* over solid caustic potash and concentrated sulphuric acid. A very viscous amorphous mass was left, which, by continued scratching, finally became solid. When dissolved in warm acetone and allowed to cool the sulphate separated in crystalline plates which melted at about 139°.

An analysis was made by titrating with barium chloride, potassium bichromate, and ammonia.

0.1920 gram substance required 9.65 cc. tenth-normal $BaCl_2$.

	Calculated for $C_{16}H_{22}N_4O_6S$.	Found.
SO_4	24.11	24.14

Action of Dilute Hydrochloric Acid on Methyl Phenylisourea.

Methyl phenylisourea, when heated with 8 per cent hydrochloric acid (1.1 mol.) for four hours at 100°, gave much methyl chloride and monophenylurea (melting-point 147°). The reaction takes place according to

$$C_6H_5NHC(:NH)OCH_3 + H_2O + HCl \rightarrow CH_3Cl + C_6H_5NHCONH_2 + H_2O,$$

the water, although in large excess, taking no part in the reaction.

Action of Benzoyl Chloride on Methyl Phenylisourea.

Two and a half grams (1½ mol.) methyl phenylisourea were dissolved in ten times the volume of alcohol-free ether, 4 grams (2 mol.) of a 33 per cent caustic potash solution added, and to the whole, kept cold by ice-water, 2 grams (1 mol.) benzoyl chloride, dissolved in 7 grams ether, added. The

flask was vigorously shaken for half an hour or until all the benzoyl chloride had been used up. The ether solution was washed once with water to get rid of the excess of alkali, once with very dilute hydrochloric acid to take out all unused methylphenyl isourea, and finally, after washing three more times with water, dried with anhydrous sodium sulphate. Evaporation of the ether solution left an oil mixed with a very little solid. The oil was at once taken up with 65 cc. dry ligroin (boiling-point 40° to 60°), and on evaporation of this ligroin solution *in vacuo* over paraffin and sulphuric acid to half its original volume, crystals (B) separated. The ligroin solution remaining was poured into a second beaker, and further evaporation left an oil mixed with some crystals. On redissolving the oil in ligroin and evaporating again a clear oil (A) was obtained. That the oil and crystals are isomeric benzoyl derivatives of methyl phenylisourea, the oil having the benzoyl and phenyl groups bound to different nitrogen atoms, and the solid having these groups attached to the same nitrogen atom will now be shown.

Symmetrical Methyl Benzoylphenylisourea,[1] $C_6H_5CONHC(:NC_6H_5)OCH_3$.—0.26 gram of the oil (A) heated in a current of dry hydrogen chloride began to evolve methyl chloride at about 35°. The urea left in the tube, after recrystallizing once from alcohol, melted at 203° to 204°; mixed with the synthetic[2] symmetrical benzoylphenylurea the melting-point was still 203° to 204°. The decomposition,

$$C_6H_5CONH.C(:NC_6H_5)OCH_3 + HCl \rightarrowtail C_6H_5CONH.CO.NHC_6H_5 + CH_3Cl,$$

shows that the oil is the symmetrical methyl benzoylphenylisourea. Analysis of the oil gave the following figures:

0.1711 gram substance gave 16.0 cc. moist nitrogen at 17° and 751.8 mm.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.05	10.77

The interesting observation was made that the symmetrical

[1] Wheeler and Johnson: *Loc. cit.*

[2] Kuhn: Ber. d. chem. Ges., 17, 2881.

methyl benzoylphenylisourea forms salts with bases as well as with acids. A little of the oil was dissolved in alcohol and water added until the solution had become quite turbid. Addition of a few drops of a solution of caustic potash (1 : 2) caused the turbidity to disappear.

On adding a little acid to this clear solution it again became turbid, and now by adding either more acid or more alkali the turbidity could be caused to disappear. The silver salt can be formed by addition of silver nitrate to a solution of the potassium salt. The study of the constitution of these and analogous salts will be undertaken in the near future.

Asymmetrical Methyl Benzoylphenylisourea, $(C_6H_5CONC_6H_5)C(:NH)OCH_3$.—The solid isomer (B) was washed several times with ligroin (boiling-point 40° to 60°) and dried on a clay plate *in vacuo* over paraffin. It then melted at 64° to 65°.

0.1661 gram substance gave 15.7 cc. moist nitrogen at 16° and 750 mm.

	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
N	11.05	10.91

When treated the same as the isomeric oil (A) this compound also formed a potassium and a silver salt.

Asymmetrical Benzoylphenylurea, $C_6H_5CONC_6H_5.CO.NH_2$.—Some of this solid methyl benzoylphenylisourea heated in a current of dry hydrogen chloride evolved methyl chloride quantitatively according to

$$C_6H_5CONC_6H_5.C(:NH)OCH_3 + HCl \rightarrow CH_3Cl + C_6H_5CONC_6H_5.CO.NH_2.$$

The residue left in the tube after recrystallizing twice from alcohol melted at about 146°, but the liquid formed on melting was always cloudy, as if on melting there was decomposition. That the residue was not monophenylurea (melting-point 147°) was shown by the fact that a mixture of the two melted 20° lower. The unsymmetrical benzoylphenylurea not being known, the compound was identified by analysis:

I. 0.2170 gram substance gave 0.5570 gram CO_2. [H_2O lost.]

II. 0.1478 gram substance gave 15.6 cc. moist nitrogen at 16°.5 and 747.5 mm.

	Calculated for $C_{14}H_{12}N_2O_2$.	Found. I.	II.
C	69.94	70.00	....
H	5.05	lost	....
N	11.69	....	12.12

Symmetrical benzoylphenylurea melts 60° higher; *viz.*, at 204°.

Methyl (Sym) Diphenylisobiuret, $C_6H_5NH.C(OCH_3) : NCONHC_6H_5$.—This compound is formed on mixing cold absolute ether solutions of methylphenylisourea and phenyl isocyanate[1] (slightly less than one equivalent), a solid separates and the precipitation is completed by the addition of low-boiling ligroin, in which the isobiuret is almost insoluble. After recrystallizing the compound by dissolving it in ether and again precipitating it with ligroin, its melting-point was found to be 111°. The substance is soluble in chloroform, alcohol, and ether.

0.1490 gram substance gave 20.5 cc. moist nitrogen at 17°.5 and 747.4 mm.

	Calculated for $C_{15}H_{15}N_3O_2$.	Found.
N	15.64	15.72

The isobiuret is formed according to

$$C_6H_5NHC(:NH)OCH_3 + C_6H_5NCO \rightarrow C_6H_5NHC(OCH_3) : NCONHC_6H_5.$$

Its structure was determined as follows: Dry hydrogen chloride passed into a solution of the substance in cold ether, to which a little alcohol had been added to increase the solubility of the base, gave a precipitate of the hydrochloride. On drying this salt *in vacuo* it lost methyl chloride spontaneously, giving a compound free from chlorine. A portion which had been dried over night in a vacuum desiccator, when recrys-

[1] Prepared according to the method of Dains: J. Am. Chem. Soc., 21, 165 (Cf. Lengfeld and Stieglitz: This JOURNAL, 16, 71; and Folin: *Ibid.*, 19, 336).

tallized once from alcohol, gave a product melting at 209°.5 to 210°. Hofmann[1] describes *α*-diphenylbiuret,

$$(C_6H_5NH.CO)_2NH,$$

as melting at 210°. Decomposition was effected therefore according to

$$C_6H_5NH.C(.OCH_3) : NCONHC_6H_5 + HCl \rightarrow C_6H_5NHCONHCONHC_6H_5 + CH_3Cl.$$

Ethyl Tolylisourea (*Ethyl o-Tolylimidocarbamate*), $NH_2C(:NC_7H_7)OC_2H_5$.—The behavior of *o*-tolylcyanamide towards alcohol showed that the peculiarities of the conditions for adding alcohol to phenylcyanamide are characteristic of the group of alphylcyanamides and not restricted to the one cyanamide. Like phenylcyanamide, it did not respond to the treatment with alcohol and sodium ethylate, but was readily converted into the ether by treatment with a large excess of alcohol and a little hydrogen chloride.

o-Tolylcyanamide has previously been described by Voltmer,[2] who obtained it by the action of hydroxylamine on the mustard oil. It was prepared in quantity by desulphurizing *o*-tolylthiourea[3] with an alkaline solution of lead acetate according to the method used by Hofmann[4] with phenylthiourea. Its melting-point was found to agree with that given by Voltmer.

o-Tolylcyanamide (1 mol.) was treated with absolute alcohol (10 mol.) and hydrogen chloride (2 mol.). After standing two days the contents of the flask were worked up according to the same method of procedure that was applied to ethyl phenylisourea. For purification the crude oil was dissolved in ligroin (40° to 60°), filtered from a small mass of *o*-tolylurea crystals, the ligroin distilled off, and the oil fractioned twice *in vacuo*. The isourea boils at 144° (19 mm.). It could not be solidified. In its solubilities, taste, and odor it is very similar to the phenylisourea ethyl and methyl ethers.

[1] Ber. d. chem. Ges., 4, 265.

[2] *Ibid.*, 24, 381.

[3] Prepared by heating together *o*-toluidine hydrochloride and ammonium sulphocyanide.

[4] Ber. d. chem. Ges., 18, 3220.

Analysis of the isourea ether gave the following figures:

0.2101 gram substance gave 29 cc. moist nitrogen at 21° and 749.5 mm.

	Calculated for $C_{10}H_{14}N_2O$.	Found.
N	15.76	15.57

On heating in a current of dry hydrogen chloride some of the oil contained in a tube connected with an azotometer, an evolution of gas took place as low as 56°. The gas was identified as ethyl chloride by its green-colored flame. The solid remaining in the tube after recrystallization from hot water melted at 190°. As this is a higher melting-point than the literature[1] gives for mono-*o*-tolylurea which should have been formed in the reaction, the urea was prepared from *o*-toluidine hydrochloride and potassium cyanate. Crystallized from hot water it melted at 190°; mixed with that obtained from the isourea ether the melting-point was not changed.

Ethyl o-Tolylisourea Chlorplatinate, $(C_{10}H_{15}N_2O)_2PtCl_4$.—On adding an excess of an alcoholic solution of chlorplatinic acid to a solution of the tolyl ether in absolute ether the orange-yellow chlorplatinate separates at once. Washed with absolute ether and dried *in vacuo* the crystals were found to melt with evolution of a gas at 177°. Under the microscope the crystal form is seen to be that of hexagonal prisms.

0.3895 gram substance gave 0.0986 gram platinum.

	Calculated for $C_{20}H_{30}N_4O_2PtCl_6$.	Found.
Pt	25.43	25.31

Action of Dilute Hydrochloric Acid on Ethyl o-Tolylisourea.

Ethyl tolylisourea showed the same behavior towards dilute hydrochloric acid as did the phenylisourea ethers. Heated with slightly more than the equivalent amount of 8 per cent hydrochloric acid for four hours at 100° it gave much ethyl chloride and *o*-tolylurea (melting-point 190°).

[1] Voltmer: Ber. d. chem. Ges., 24, 382, gives 189°; Beilstein's Handbuch (Cosack: Ber. d. chem. Ges., 13, 1089) gives 185°.

Methylphenylcyanamide (*methyl cyanilide*),[1] $C_6H_5N(CH_3).CN$, was prepared in order to obtain and study unsymmetrically disubstituted isourea ethers, $R_2NC(:NH)OR$, and to see if an alkyl phenylcyanamide, an undoubted imido nitril, would conduct itself in the same way towards alkaline and acid alcohol solutions as phenylcyanamide (see p. 214).

Eight and three-tenths grams (1 mol.) of methyl phenylthiourea[2] were added to 35 cc. (4 mol.) of a hot solution of caustic potash (1 : 2) in which it only partially dissolved. To the mixture a hot concentrated solution of 23 grams (4 mol.) lead acetate was then added and the whole heated in the water-bath for a few minutes.

The beaker was cooled, its contents extracted several times with ether, and the ether solution dried with fused calcium chloride. On distilling off the ether in the water-bath, an amount of very nearly pure methylphenylcyanamide, corresponding to a yield of 82 per cent of the theory, was obtained. Distillation with steam gave it in beautiful colorless plates having a spicy nitril odor and melting at 30°.5.

Methylphenylcyanamide is readily soluble in all the ordinary organic solvents and in the concentrated mineral acids, but practically insoluble in dilute acids. It can be obtained pure by crystallization from a large volume of water or by distillation with steam.

0.2045 gram substance gave 0.5443 gram CO_2 and 0.1150 gram H_2O.

	Calculated for $C_6H_5NCH_3CN$.	Found.
C	72.64	72.59
H	6.11	6.30

Asymmetrical Ethyl Methylphenylisourea (*Ethyl Imidophenylmethylcarbamate*), $(C_6H_5NCH_3)C(:NH)OC_2H_5$.—In contrast with the behavior of phenylcyanamide towards sodium ethylate and alcohol its methyl derivative is most readily converted into the above ether by slowly adding a solution of 13.2 grams

[1] This has since been prepared by Wallach (Ber. d. chem. Ges., 32, 1872) from methylaniline and bromcyanogen, and by Traube and Wedelstädt (Ber. d. chem. Ges., 33, 1384) by methylating phenylcyanamide in the presence of sodium alcoholate. Wallach describes it as melting at 28° and boiling at 136° (10 mm.).

[2] Gebhardt: Ber. d. chem. Ges., 17, 2094.

(1 mol.) methylphenylcyanamide in 50 grams absolute alcohol in the cold to 32 grams absolute alcohol, in which 2.5 grams (1.1 atoms) sodium has been dissolved. Scarcely any rise of temperature is observed, while in a similar reaction between sodium alcoholate and carbodiphenylimide[1] very much heat is evolved. The mixture was allowed to stand two days and then carbon dioxide was run into it for fifteen minutes, the mass poured into 0.5 liter of water, and the whole extracted four times with ether. The farther treatment was the same as for the preparation of ethylphenylisourea (see above). Sixteen grams of the slightly colored crude isourea ether, *i. e.*, 90 per cent of the theoretical yield, was obtained. The boiling-point of the pure ether was found to be 137° (21 mm.)

0.4004 gram substance gave 56.1 cc. moist nitrogen at 22°.5 and 745.6 mm.

	Calculated for $C_{10}H_{14}N_2O$.	Found.
N	15.76	15.61

Methylphenylcyanamide, heated in a sealed tube with a slight excess of absolute alcohol, did not give a trace of the isourea ether, whereas carbodiphenylimide gives a nearly quantitative yield of the corresponding ether under the same treatment.

Some success attended the treatment of the cyanamide with 10 molecules of alcohol and 2 molecules of hydrogen chloride, but the reaction proceeds very slowly, reaching completeness only after several weeks, while with phenylcyanamide the action was complete in two days.

On heating ethyl methyl phenylisourea in a current of dry hydrogen chloride ethyl chloride was evolved. The residue left in the tube, after crystallization from low-boiling ligroin, melted at 81°, and mixed with the synthetically[2] prepared methyl phenylurea the melting-point was still 81°. The reaction took place according to

$$C_6H_5NCH_3.C(:NH)OC_2H_5 + HCl \rightarrow C_2H_5Cl + C_6H_5NCH_3CONH_2.$$

[1] Stieglitz: Ber. d. chem. Ges., 28, 573.
[2] Gebhardt: *Ibid.*, 17, 2095.

Ethyl Methylphenylisourea Chlorplatinate, $(C_{10}H_{15}N_2O)_2PtCl_6$, made by adding a slight excess of an absolute alcoholic solution (1 : 1) of chlorplatinic acid to an ether solution of the ethyl methyl phenylisourea, forms brownish-yellow crystals.

0.4288 gram substance gave 0.1097 gram platinum.

	Calculated for $C_{20}H_{30}N_4O_2PtCl_6$.	Found.
Pt	25.43	25.58

The platinum salt melts at 160° with evolution of a gas, darkening in color a few degrees below its melting-point. While the form of the individual crystal could not be determined by the use of the microscope, that of the crystal aggregate is peculiar and distinctive, the crystals joining together to form an aggregate, which, under the microscope, has an appearance similar to that of a pine tree.

Action of Dilute Hydrochloric Acid on Ethyl Methylphenylisourea.

With the ethyl ether of methylphenylisourea, as in the case of the phenylisourea ethers, the first action, when heated with dilute hydrochloric acid, is the formation of alkyl chloride and a urea according to

$$C_6H_5N(CH_3)C(:NH)OC_2H_5 + HCl \rightarrow C_6H_5N(CH_3)CONH_2 + C_2H_5Cl.$$

Experiment showed that, in addition to this fundamental reaction, the dilute acid brought about some saponification of the methylphenylurea with formation of methylaniline, as follows:

$$C_6H_5N(CH_3)CONH_2 + H_2O \rightarrow C_6H_5.NH.CH_3 + NH_3 + CO_2.$$

The methylaniline thus formed was, to a very small extent, ethylated by the ethyl chloride present with formation of methylethylaniline,

$$C_6H_5.NH.CH_3 + C_2H_5Cl \rightarrow C_6H_5N(C_2H_5)CH_3 + HCl.$$

Ethyl methylphenylisourea (1 mol.) was heated in a sealed tube with 8 per cent hydrochloric acid (1.1 mol.) for four

hours at 100°. The tube opened with pressure due to ethyl chloride (green-edged flame). That saponification of the methylphenylurea with formation of methylaniline had taken place was shown by the fact that a portion of the liquid gave a yellow solution (nitrosomethylaniline) on the addition of a little sodium nitrite. For confirmation, parallel experiments were carried out with acid solutions of the urea ether and of the urea ether and methylaniline, only the latter giving the yellow color of the nitroso compound. The presence of a trace of methylethylaniline was shown by the yellow acid solution formed by sodium nitrite, after reduction with zinc, giving a blue color with ferric chloride and hydrogen sulphide.

Experiments carried out parallel to the one just given show that a mixture of isourea ether and methylaniline does not give the thionin color while a mixture of isourea ether, methylaniline, and dimethylaniline readily gives methylene blue. The presence of unchanged ethyl methylphenylisourea was shown by the fact that a portion of the solution, when reheated in a sealed tube at 100° for several hours, gave some more alkyl chloride. No attempt was made to isolate the methylphenylurea formed, owing to its extreme solubility.

Ethyl α-Methyl-α-diphenylisobiuret, $C_6H_5NCH_3.C(OC_2H_5) : N.CONHC_6H_5$.—Ethyl methylphenylisourea was treated with slightly less than the equivalent amount of phenyl isocyanate. The solid separating from the cold solution was filtered off and washed with cold absolute ether. Recrystallized from a little warm alcohol, it melted at 115° to 116°, softening, but not melting, about 1° lower. The biuret is formed according to

$$C_6H_5NCH_3C(: NH)OC_2H_5 + C_6H_5NCO \rightarrow C_6H_5NCH_3.C(.OC_2H_5) : NCONHC_6H_5.$$

When boiled with dilute hydrochloric acid, ethyl chloride is given off. It can be burned at the mouth of the test-tube.

The α-methyl-α-diphenylbiuret formed melted at about 102°.

Analysis of the ethyl ether gave the following figures:

0.1332 gram substance gave 16.55 cc. moist nitrogen at 17°.5 and 749.5 mm.

	Calculated for $C_{17}H_{19}N_3O_2$.	Found.
N	14.17	14.24

Action of Dilute Hydrochloric Acid on Ethyl α-Methyl-α-diphenylisobiuret.

The following experiments were made in order to determine if the action of dilute acid in the cold on a urea ether with more negative groups is the same as when the two are heated together for a shorter time.

Ethyl α-methyl-α-diphenylisobiuret was placed in a sealed tube with slightly more than the equivalent amount of normal hydrochloric acid and kept nine days at the ordinary temperature. The tube opened with no pressure, showing that only a minute quantity of ethyl chloride could be present. The solid melted at 101° to 102° after recrystallization from alcohol. It was probably the hitherto unknown biuret,

$$C_6H_5NCH_3CONHCONHC_6H_5,$$

but an analysis was not made. Ethyl alcohol could not be found in the filtrate from the biuret by the iodoform test. The presence of aniline was shown by the fact that the filtrate gave an isonitril odor when treated with chloroform and caustic potash, but did not give an alkaline gas when treated with caustic potash alone. The presence of methylethylaniline was suspected from the odor of the alkaline filtrate and proved by the thionin (methylene blue) test. The presence of these products is readily explained if the first action is considered as the formation of alkyl chloride and the biuret according to

$$C_6H_5NCH_3.COC_2H_5 : N.CONHC_6H_5 + HCl \rightarrow C_6H_5NCH_3CONHCONHC_6H_5 + C_2H_5Cl,$$

and that a part of the biuret is then saponified, producing aniline and methylaniline, as follows:

$$C_6H_5NCH_3CONHCONHC_6H_5 + 2H_2O \rightarrow C_6H_5NHCH_3 + C_6H_5NH_2 + 2CO_2 + NH_3.$$

The presence of a dialkylaniline shows that the ethyl chloride was employed in ethylation of the aniline and methylaniline according to

$$C_6H_5NH_2 + 2C_2H_5Cl \rightarrow C_6H_5N(C_2H_5)_2 + 2HCl$$

and $$C_6H_5N(CH_3)H + C_2H_5Cl \rightarrow C_6H_5N(CH_3)C_2H_5 + HCl.$$

When the isobiuret was heated with normal hydrochloric acid for three and a half hours at 100°, the products were the same as when the action took place in the cold, excepting that the tube opened with very slight pressure due to ethyl chloride. It may be concluded, therefore, that an increase of temperature does not change the course of the reaction with dilute acid, excepting that the time required for the completion of the reaction is shortened.

Methyl (asym)-Methylphenylisourea, (Methyl Imidophenylmethylcarbamate), $C_6H_5NCH_3C(:NH)OCH_3$, was prepared because it was thought that it might be a solid like some other methylisourea ethers, but the influence of the methyl group joined to nitrogen so lowers the melting-point that even at a temperature of —18° the ether could not be solidified.

The method of preparation from methylphenylcyanamide was the same as that used for the ethyl ether, but the yield was not quite so good, though satisfactory. Distilled *in vacuo* the greater part of the oil boiled at 120° at 11 mm. pressure. The identity of the body was proved by forming and analyzing the platinum salt.

0.1696 gram substance gave 0.0447 gram platinum.

	Calculated for $(C_9H_{12}N_2O)_2PtCl_6$.	Found.
Pt	26.40	26.36

Methyl (asym.)-Ethylphenylisourea (Methyl Imidophenylethylcarbamate), $C_6H_5NC_2H_5.C(:NH)OCH_3$.—The ready addition of alcohol to alkylphenylcyanamides by means of sodium alcoholate was confirmed by the action of sodium methylate on ethylphenylcyanamide.

Ethylphenylcyanamide has been prepared by Clöez and Cahours[1] from ethylaniline by the action of chlorcyanogen. For its preparation in quantity it was found best to desulphurize ethyl phenylthiourea[2] with alkaline lead acetate solu-

[1] Ann. Chem. (Liebig), **90**, 94.
[2] Gebhardt: Ber. d. chem. Ges., **17**, 2094.

tion in the same manner that methylphenylcyanamide was prepared. It was found to boil at 153° (19 mm.).

0.2005 gram substance gave 33.7 cc. moist nitrogen at 16° and 748.9 mm.

	Calculated for $C_6H_5NC_2H_5CN$.	Found.
N	19.21	19.37

Methyl ethylphenylisourea was formed by treating 14.6 grams (1 mol.) ethylphenylcyanamide dissolved in 40 grams methyl alcohol with a methyl alcohol solution of sodium methylate (from 2.6 grams of sodium). The farther treatment was the same as for the preparation of its isomer, ethyl methylphenylisourea. Fractionated twice *in vacuo* the oil boiled at 126° under 15 mm. pressure. Analysis gave the following figures:

0.1604 gram substance gave 22.5 cc. moist nitrogen at 15°.5 and 747.8 mm.

	Calculated for $C_{10}H_{14}N_2O$.	Found.
N	15.76	16.18

Hydrochloride of Methyl Ethylphenylisourea, $C_6H_5NC_2H_5C(:NH)OCH_3.HCl$.—Dry hydrogen chloride was passed into a solution of the isourea ether in absolute ether, the precipitated hydrochloride filtered off, and after washing with ether, dried *in vacuo* over caustic potash and concentrated sulphuric acid. Methyl ethylphenylisourea hydrochloride is insoluble in benzene, ligroin, and ether, but soluble in other organic solvents. Its water solution is neutral to litmus and to methyl orange. The salt was found to melt at 107° with evolution of methyl chloride.

0.1240 gram substance required 5.80 cc. tenth-normal $AgNO_3$ (chromate indicator).

	Calculated for $C_{10}H_{15}N_2OCl$.	Found.
Cl	16.51	16.59

Action of Dilute Hydrochloric Acid on Methyl Ethylphenylisourea.

Methyl ethylphenylisourea was heated with slightly more

than the equivalent amount of 8 per cent hydrochloric acid for four hours in the Victor Meyer water-bath. The tube opened with pressure due to methyl chloride, which burned with its characteristic green-edged flame. The contents of the tube, when treated as in the similar experiment with ethyl methylphenylisourea showed the presence of ethylaniline, methylethylaniline (only a trace), and unchanged methyl ethylphenylisourea.

II. The Oxygen Ethers of Urea.

While derivatives of the oxygen ethers of urea have been known for some time,[1] the mother-substances, the oxygen ethers of urea itself, $NH_2C(OR) : NH$, were unknown before this work was undertaken. Of the usual methods[2] which suggested themselves for preparing these interesting bodies, the addition of alcohol to cyanamide was attempted first according to

$$NH_2CN + HOR \longrightarrow NH_2C(OR) : NH,$$

because the work on the alphylcyanamides had shown the way for converting cyanamides into isourea ethers. The method proved entirely successful. It is expected, however, that since the properties of these bodies are now known they may be prepared by other convenient methods.[3]

[1] *a.* Griess: Ztschr. f. Chemie, 1867, 534; J. prakt. Chem., [2], **4**, 295; Ber. d. chem. Ges., **15**, 448.

b. Cyclic isoureas, Gabriel: Ber. d. chem. Ges., **22**, 1150; **28**, 2937; Hirsch: Ber. d. chem. Ges., **23**, 966; Menne: Ber. d. chem. Ges., **33**, 658.

c. Cyclic isoureas from imidocarbonic esters, Sandmeyer: Ber. d. chem. Ges., **19**, 862; Seliwanow: Ber. d. chem. Ges., **26**, 425.

d. Uric acid ethers, E. Fischer: Ber. d. chem. Ges., **17**, 332, 335.

e. Ethyl isocarbanilide, Lengfeld and Stieglitz: Ber. d. chem. Ges., **27**, 926; this JOURNAL, **17**, 112. Stieglitz: Ber. d. chem. Ges., **28**, 573.

f. Bromdiphenylisoureas. Hantzsch and Mai: Ber. d. chem. Ges., **28**, 983.

g. Isocarbanilides, Dains: J. Am. Chem. Soc., **21**, 136.

h. Benzoyl alkylisoureas, Dixon: J. Chem. Soc. (London), 1899, 380; Wheeler and Johnson: This JOURNAL, **24**, 217.

i. Isourea ethers, Stieglitz and McKee: Ber. d. chem. Ges., **32**, 1494; **33**, 807, 1517.

[2] See preliminary reports, Stieglitz and McKee: Ber. d. chem. Ges., **32**, 1494: **33**, 807, 1517.

[3] Other methods will be tried in this laboratory as soon as possible, *e. g.* the action of alkyl halides on silver ureas, the preparation of cyanic ethers, CN.OR, and the addition of ammonia to them, the action of diazourethane on urea, and the saponification of benzoylmethylisourea, etc. J. STIEGLITZ.

Methylisourea Hydrochloride (*Hydrochloride of Methyliminocarbamate*), $NH_2C(:NH)OCH_3.HCl$.—Preliminary experiments showed at once that methylisourea is formed when cyanamide is treated with absolute methyl alcohol and dry hydrogen chloride. The residue, left on evaporation of the alcoholic solution in a vacuum desiccator over concentrated sulphuric acid and solid caustic potash, gave, when heated in a current of dry hydrogen chloride, some methyl chloride and urea, but not at all in quantities corresponding to a nearly pure compound. Great difficulties were met in obtaining the ether and its salts in a pure condition. On the one hand, a large number of experiments were made to find the best conditions for preparing the hydrochloride and, on the other hand, to obtain a pure product by fractional crystallization of the hydrochloride and by fractional distillation of the free base. Success in the first line made it unnecessary to follow the second. Passing over all the preliminary work, the method will be described which first gave the pure hydrochloride and which is suitable for preparing small quantities of the substance, and then the mode of preparation on a large scale will be briefly given.

Forty-three grams (1 mol.) of well-dried silver cyanamide,[1] 80 grams (15 mol.) absolute methyl alcohol, and 19 grams (3.1 mol.) dry hydrogen chloride, were allowed to react for five to eight days. At the end of this period, when the solution no longer gave the test for cyanamide with silver nitrate and ammonia, the silver chloride was filtered off and the solution evaporated to dryness *in vacuo* over sulphuric acid and solid caustic potash. A crust, containing most of the impurities, was generally left on the sides of the beaker. The greater portion of the residue consisted of almost pure, well-formed, quadrangular prisms of methylisourea hydrochloride formed according to

$$CN_2Ag_2 + CH_3OH + 3HCl \rightarrow NH_2C(:NH)OCH_3,HCl + 2AgCl.$$

The second method of forming the hydrochloride, which is

[1] Walther: J. prakt. Chem., [2], 54, 510.

to be preferred, if a large amount of the compound is desired, is as follows: 8.7 grams dry hydrogen chloride (1.08 mol.) is passed into a well-cooled solution of 10.5 grams cyanamide[1] (1 mol.) in 200 grams methyl alcohol (25 mol.) which has been distilled over sodium. After standing two days the reaction is complete, for no precipitate of silver cyanamide forms on testing a portion of the solution with ammonia and silver nitrate. The solution is concentrated in a distilling flask under reduced pressure at 35° until crystals begin to appear in the liquid. The evaporation is completed in a vacuum desiccator over concentrated sulphuric acid and caustic potash. The hydrochloride is obtained in about the same state of purity as when it is prepared by the first method.

Syntheses by means of sodium alcoholate under various conditions were tried, but only traces of the desired isourea ether were obtained.

From a preparation of the salt from silver cyanamide some of the more perfect crystals were taken, washed with absolute alcohol, powdered, and after drying *in vacuo* over sulphuric acid and solid caustic potash for three days to remove any excess of hydrochloric acid analyzed (Analysis I). The alcohol used in washing the crystals for Analysis I also left, on evaporation, pretty crystals of pure hydrochloride (Analysis II). The crude salt prepared from cyanamide was dissolved in a small volume of absolute alcohol warmed to a temperature of 55° to 60°. When cooled to −10° this alcoholic solution gave crystals of the pure methylisourea hydrochloride (Analyses III and IV).

I. 0.1107 gram substance required 10.05 cc. tenth-normal $AgNO_3$ (chromate indicator).

II. 0.1149 gram substance required 10.41 cc. tenth-normal $AgNO_3$.

III. 0.1001 gram substance required 9.03 cc. tenth-normal $AgNO_3$.

[1] Volhard: J. prakt. Chem., [2], 9, 25. It was found better after filtering from the mercuric sulphide and neutralizing with acetic acid to distil off almost all the water from the cyanamide at a pressure of about 25 mm. instead of evaporating on the water-bath to a small volume.

IV. 0.0785 gram substance gave 18.2 cc. moist nitrogen at 25° and 748.5 mm.

	Calculated for $C_3H_8N_2O.HCl$.	Found. I.	II.	III.	IV.
Cl	32.05	32.18	32.12	32.04	....
N	25.39	....	....	....	25.62

Besides proving the identity and purity of the new salt, the analyses brought out the noteworthy fact that methylisourea forms only a stable monohydrochloride.[1] This salt is perfectly neutral.[2] A little of the hydrochloride dissolved in water did not change the tint of neutral litmus paper. That an unstable higher hydrochloride probably exists is shown by the fact that the powder used for Analysis I, after having been in the desiccator but a short time gave, on analysis, 34.74 per cent chlorine. Its aqueous solution reacted strongly acid towards litmus and methyl orange.

Methylisourea hydrochloride is very soluble in water and in methyl alcohol, not quite so soluble in ethyl alcohol, and insoluble in ether. Heated in a melting-point tube, it melts at 132° to 133° with evolution of methyl chloride. When it was heated in a current of hydrogen chloride it melted at 130°, forming methyl chloride quantitatively; the residue, dissolved in water, gave, with a few drops of nitric acid, a good yield of urea nitrate melting at 161°. Mixed with synthetic urea nitrate the melting-point remained unchanged. These reactions and the method of formation prove the constitution of the substance to be that of the hydrochloride of the methyl oxygen ether of urea:

$$NH_2CN + CH_3OH + HCl \rightarrow NH_2C(:NH)OCH_3.HCl;$$
$$NH_2C(:NH)OCH_3.HCl \rightarrow NH_2CONH_2 + CH_3Cl.$$

Methylisourea Chlorplatinate, $[NH_2C(:NH)OCH_3]_2H_2PtCl_6$. —Some of the crude crystals of the hydrochloride were washed with a small amount of absolute alcohol and then dissolved in a little of the alcohol and an excess of an alcoholic solution of chlorplatinic acid added. As no crystals separated on cooling

[1] Stieglitz: This JOURNAL, 21, 105.
[2] *Ibid.*, 106.

the solution to —10°, absolute ether was added. A precipitate formed which was filtered and washed with dry ether with the aid of the filter-pump. After drying *in vacuo* over concentrated sulphuric acid it was analyzed.

0.1917 gram substance gave 0.0668 gram platinum.

II. 0.2026 gram substance gave 17.5 cc. moist nitrogen at 12° and 754.0 mm.

	Calculated for $(C_2H_7N_2O)_2PtCl_6$.	Found. I.	II.
Pt	34.92	34.85	....
N	10.07	....	10.20

The chlorplatinate is soluble in water, methyl and ethyl alcohols, and acetone. It crystallizes in long, lemon-yellow needles, which on heating become orange at about 120°, and melt at 178° with evolution of a gas.

Methylisourea,[1] $NH_2C(:NH)OCH_3$.—Three and two-tenths grams of methylisourea hydrochloride were placed in a flask with about 1 gram water and 20 cc. alcohol-free ether, and the whole cooled to —12°. Powdered caustic potash was then added in small portions, but in large excess (20 to 25 mol.). The ether was decanted off, fresh ether added, and brought into good contact with the nearly solid mass under it by rubbing with a glass rod, decanted off, and the addition of fresh ether repeated a third and a fourth time. The resulting ether solution was shaken five minutes with anhydrous sodium sulphate, filtered by means of a siphon filter, and most of the ether distilled off in the water-bath. On scratching with a glass rod the concentrated ether solution (cooled to —10°), a crystalline precipitate of the free methylisourea resulted. If the hydrochloride used was of good quality, the yield of pure methylisourea is practically quantitative. If impure hydrochloride is used, the product is best purified by distilling *in vacuo*. Recrystallized from absolute ether the melting-point was 44° to 45°.

0.2430 gram substance gave 0.2875 grams CO_2 and 0.1793 grams H_2O.

[1] Other names are methyl imidocarbamate, methyl imidoamidoformate, and methoxyformamidine.

	Calculated for $NH_2.COCH_3:NH$.	Found.
C	32.37	32.27
H	8.17	8.27

Methylisourea distilled *in vacuo*, best in an Anschütz flask, boils at 82° at 9 mm. At atmospheric pressure it does not distil undecomposed. It has a fishy, amine-like odor and it is very volatile with the vapors of alcohol and of ether. This volatility is not unexpected when the relation of methylisourea, $NH_2C(:NH)OCH_3$, to methylurethane, NH_2COOCH_3, which is extremely volatile, is considered. Methylisourea is a very powerful base; its aqueous solutions react strongly alkaline and, as described above, it exactly neutralizes 1 molecule of hydrochloric acid, the monochloride giving a neutral solution with water. In accordance with that fact it was found that the base could be titrated against hydrochloric acid. The following determinations were made with freshly distilled methylisourea, using tenth-normal hydrochloric acid and methyl orange as indicator.

I. 0.1410 grams required 18.87 cc. tenth-normal HCl; calculated 19.02 cc.

II. 0.1488 grams required 19.94 cc. tenth-normal HCl; calculated 20.07 cc.

III. 0.0996 grams required 13.36 cc. tenth-normal HCl; calculated 13.43 cc.[1]

Considering the hygroscopic character of the base the titrations are as close to the theory as could be expected.

Attempts were made to isolate the free isourea ether by treating a methyl alcohol solution of the hydrochloride with the theoretical amount of sodium methylate, and, after filtering from the precipitated sodium chloride, distilling the resulting solution.[2] In each trial a large amount of the base went over with the methyl alcohol, making the distillate strongly alkaline. After distilling off the alcohol at reduced pressure a little oil was left, a few drops of which distilled on

[1] This titration was made by placing a measured amount of acid in the flask, weighing, adding isourea ether, and weighing again, and titrating the excess of acid with tenth-normal sodium hydroxide.

[2] Lobry de Bruyn's method for preparing free hydroxylamine. (Rec. trav. chim. Pays-Bas., II., 18).

heating *in vacuo*, but the greater portion suddenly decomposed, giving a white solid.

Methylisourea exposed to the air took up sufficient moisture within a few hours to dissolve it. After a couple of days all solvent had disappeared, leaving a solid, the greater part of which was the carbonate of the base, as was shown by identifying the gas evolved when it was treated with dilute acid. No urea could be detected by the furfurol test. A small amount of a solid insoluble in water and in dilute acid was formed, but it was not identified. The total weight of solid obtained was only half that of the methylisourea taken, owing to the great volatility of the isourea ether.

Action of Dilute Hydrochloric Acid on Methylisourea.

When heated with dilute aqueous hydrochloric acid, the simple isourea ethers, like their phenylated derivatives, give urea and an alkyl chloride. But at the same time, to a very small extent (about 1 per cent) a decomposition into methyl urethane[1] and ammonium chloride takes place according to

$$NH_2C(:NH)OCH_3 + H_2O + HCl \rightarrow NH_2COOCH_3 + NH_4Cl.$$

This decomposition is especially worthy of note from its correspondence to that of the imidoethers when they are treated with dilute acid.

Methylisourea and slightly more than the equivalent amount of normal hydrochloric acid were heated for three and a half hours in a Victor Meyer water-bath. The tube was opened to allow the escape of methyl chloride, resealed, and heated for three hours longer. On opening the second time there was again pressure due to alkyl chloride. Evidently the decomposition of the hydrochloride into methyl chloride and urea is a slow process, showing the salt to be a comparatively stable one even at high temperatures. In the time required to decompose the chloride, much of the urea formed is saponified to ammonia and carbonic acid, and the ammonia partly converted into methylamine. The solution was found to be alkaline. A portion of it was neutralized with a few drops of dilute nitric acid and titrated with silver nitrate. Fifty per cent of

[1] Proved exactly in the case of ethylisourea.

the chlorine originally in the solution was found still present in the ionic condition.

A second portion of the solution, when tested for methyl alcohol by the delicate resorcinol test,[1] gave negative results. The third and larger part of the solution was evaporated to dryness *in vacuo* over concentrated sulphuric acid. The solid remaining was extracted twice with absolute ether and the ether solution evaporated. A small amount of a solid was left. It melted at 43° and had the solubilities of methylurethane. The amount was too small to recrystallize, but from its low melting-point it was probably methylurethane, NH_2COOCH_3 (melting-point 52°). The solid which had been extracted with ether was dissolved in a little water and a few drops of nitric acid added; the resulting abundant precipitate was identified as urea nitrate.

Benzoylmethylisourea (*Methyl Imidobenzoylcarbamate*), $C_6H_5CONHC(:NH)OCH_3$,[2] was prepared by dissolving methyl isourea hydrochloride in an excess of a 10 per cent solution of caustic potash, adding slightly less than the equivalent amount of benzoyl chloride and shaking vigorously until no acid chloride remained unaffected. The benzoylmethylisourea was filtered off and purified by dissolving it in a little methyl alcohol and fractionally precipitating it by the careful addition of water to the cold solution. This recrystallized substance forms monoclinic prisms melting at 76°.5.[3] The yield was almost quantitative.

I. 0.2802 gram substance gave 0.6238 gram CO_2 and 0.1464 gram H_2O.

II. 0.1536 gram substance gave 21.5 cc. moist nitrogen at 18° and 738.4 mm.

	Calculated for $C_9H_{10}N_2O_2$.	Found. I.	Found. II.
C	60.61	60.72	....
H	5.67	5.86	....
N	15.76	....	15.77

[1] Mulliken and Scudder: This JOURNAL, **21**, 266.

[2] Vide Dixon: J. Chem. Soc. (London), 1899, 380; Wheeler and Johnson: This JOURNAL, **24**, 217.

[3] Dixon gives the melting-point as 74° to 75°, Wheeler as 77°.

Benzoylmethylisourea is readily soluble in alcohol and ether. It acts both as a base and as an acid, dissolving easily in acids as well as in alkalies.[1] From the solution in alkalies careful addition of acid reprecipitates the benzoylmethylisourea, which was identified by its crystal form, melting-point, and behavior towards boiling dilute hydrochloric acid (see below). It also forms a silver salt. None of the salts with metals has been prepared as yet in a pure condition. It is intended to investigate them further. It is probable that they have the interesting constitution

$$C_6H_5C(OK) : N.C(: NH).OCH_3.$$

The solution of benzoylmethylisourea in dilute alcohol reacts neutral to litmus, and in view of the fact that it has both basic and acid properties the free substance may be a salt analogous to amidoacetic acid.

Action of Dilute Hydrochloric Acid on Benzoylmethylisourea.

Benzoylmethylisourea was dissolved in slightly more than 1 molecule normal hydrochloric acid and the tube heated in the Victor Meyer water-bath three hours and a half. The tube opened with very slight pressure, due to methyl chloride, as shown by the gas burning with a green flame. The precipitate was separated into benzoylurea and benzoic acid by dissolving the latter in sodium carbonate. The benzoylurea[2] melted at 200° and was soluble in caustic alkalies; the benzoic acid melted at 120°, and when mixed with some of known constitution gave the same melting-point. The filtrate gave no trace of methyl alcohol by the resorcinol test. On making the filtrate alkaline with caustic potash a gas was evolved, which was strongly alkaline to litmus. That this gas was at least in part methylamine was shown by the fact that another portion of the filtrate, when treated with chloroform and caustic potash, gave a strong isonitril odor.

The amount of methyl chloride obtained by the action of aqueous hydrochloric acid on the benzoylmethylisourea

[1] The latter fact does not seem to have been observed by Dixon and Wheeler.

[2] Zinin: Ann. Chem. (Liebig), 92, 404, describes benzoylurea as melting at about 200°. Wheeler, *Loc. cit.*, gives the melting-point at 214°.

seemed so unusually small that, in consequence of the presence of methylamine, I was led to suspect that methyl chloride was really formed in large quantities, as in the case of other urea ethers, but had been largely used up in methylating some ammonia formed by decomposition of the urea. This view was fully confirmed by repeating the experiment and heating the isourea ether with dilute hydrochloric acid for only twenty minutes. The tube now opened with great pressure and gave abundant methyl chloride. Benzoylmethylisourea is therefore decomposed in the first instance by dilute hydrochloric acid[1] like the other isourea ethers into alkyl chloride and a urea according to the equation:

$$C_6H_5CONHC(:NH)OCH_3 + HCl \rightarrowtail C_6H_5CONHCONH_2 + CH_3Cl.$$

For purposes of comparison benzimidoethyl ether was heated for several hours with normal hydrochloric acid under the same conditions and gave, as expected, no trace of ethyl chloride, but only ethyl benzoate and ammonium chloride according to

$$C_6H_5C(:NH)OC_2H_5 + HCl + H_2O \rightarrowtail C_6H_5COOC_2H_5 + NH_4Cl.$$

With normal hydrochloric acid at the room temperature benzoylmethylisourea gave, after eight days, the same products as at higher temperatures.

It is seen that, in spite of the presence of the strongly negative benzoyl group, and of the weak basic properties of the substance, the decomposition is not affected by the water present—hydrolysis seems to play no rôle in this action as in

[1] Wheeler and Johnson (This JOURNAL, **24**, 217), working with a different object in view, found that benzoylmethylisourea is rapidly decomposed in the same way by gently warming it with 20 per cent hydrochloric acid. In the above experiment very dilute acid was always used with a view of detecting a possible hydrolysis of the urea ether salts, corresponding to the hydrolytic decomposition of the imidoethers. A large excess of acid would suppress hydrolysis and favor the formation of the decomposition-products of the hydrochlorides (Stieglitz: This JOURNAL, **21**, 106). As a matter of fact, Mr. McCracken, working under the direction of Dr. Stieglitz, was able to prove that imidoethers, like methyl imidobenzoate, readily give alkyl chlorides in quantity when heated with concentrated *aqueous* hydrochloric acid in place of the dilute acid. The results of Mr. McCracken's investigation, carried out early in 1899, will be published later, the work having been temporarily interrupted.

the case of the imidoesters. This is the more striking since the solution of the hydrochloride is strongly acid, *i. e.*, water dissociates the salt into the free base and free acid, but according to the observed products of decomposition it can have no further action on the free base. This conclusion is in complete agreement with Dixon's experiments with benzoylmethylisourea,[1] according to which the compound could be heated with 10 parts of water to 105° to 125° without any sign of change. I confirmed this important point for the question of hydrolysis by heating the body for three hours with five times its weight of water in a sealed tube in a Victor Meyer water-bath. On opening the tube, the isourea ester was recovered unchanged, no interaction with the water having occurred.

Methyl Phenylisobiuret (*Methyl Phenylureidoimidoformate*, $(C_6H_5NHCON:)COCH_3.NH_2$.[2]—Six-tenths of a gram (1 mol.) of methylisourea hydrochloride was dissolved in a very little water, an equivalent amount of a strong solution of caustic potash added, and to the resulting solution 0.6 gram (0.9 mol.) phenyl isocyanate added. After shaking the cold solution until no isocyanate odor could be detected, the solid which had separated was taken up with a little ether. The ether solution was washed three times with small amounts of water to get rid of any unchanged methylisourea, and dried with anhydrous sodium sulphate. The drying agent was filtered off, most of the ether distilled in the water-bath, and to the concentrated ether solution, cooled to —10°, low-boiling ligroin added to precipitate the isobiuret. The yield was fair.

The phenylisobiuret can also be made by mixing absolute ether solutions of equivalent amounts of methylisourea and phenyl isocyanate. This method, however, calls for the isolation of the free methylisourea, while by the first method the hydrochloride can be used, which is a distinct advantage.

The crystals are four-sided prisms, having rather blunt pyramidal ends. They melt at 89°.5 to 90°.

0.1180 gram substance gave 22.7 cc. moist nitrogen at 20°.5 and 753.5 mm.

[1] *Loc. cit.*

[2] See page 214.

	Calculated for $C_9H_{11}N_3O_3$.	Found.
N	21.80	21.86

Hydrochloride of Methyl Phenylisobiuret, $(C_9H_{11}N_3O_3)Cl$.—Half a gram of the methyl ether was dissolved in absolute ether and dry hydrogen chloride run into the cold solution. The precipitate was filtered, washed with absolute ether, and, after drying on a clay plate *in vacuo* over sulphuric acid and solid caustic potash, analyzed.

The analysis was made by dissolving in dilute alcohol, adding tenth-normal alkali to neutrality (nearly the theoretical amount calculated for complete hydrolysis was required), and then titrating with chromate indicator and silver nitrate.

0.1750 gram substance required 7.72 cc. tenth-normal $AgNO_3$.

	Calculated for $C_9H_{12}N_3O_3Cl$.	Found.
Cl	15.43	15.64

The hydrochloride melts at 133° with evolution of a gas.

Action of Dilute Hydrochloric Acid on Methyl Phenylisobiuret.

On boiling methyl phenylisobiuret with dilute hydrochloric acid, methyl chloride was given off and burned at the mouth of the test-tube. The solution, on cooling, gave crystals which, after recrystallization, melted at 156° to 156°.5. Analysis showed it to be α-phenylbiuret, formed according to

$$C_6H_5NHCONH.COCH_3(:NH) + HCl \rightarrowtail CH_3Cl + C_6H_5NHCONHCONH_2.$$

Again, in spite of the fact that the hydrochloride is almost completely decomposed by water, water does not enter into the products of the decomposition.

α-Phenylbiuret, $C_6H_5NHCONHCONH_2$.—That the crystals melting at 156° to 156°.5 were α-phenylbiuret, as expected, was confirmed by the following analysis:

0.0793 gram substance gave 16.8 cc. moist nitrogen at 25° and 747.2 mm.

	Calculated for $C_9H_9N_3O_2$.	Found.
N	23.50	23.38

Its constitution follows from the method of preparation.

There is a phenylbiuret described in the literature,[1] but its constitution has not been determined and the properties given are general ones and are not specific enough to permit one to determine if it is identical with the one melting at 156° to 156°.5.

α-Phenylbiuret is soluble in alcohol, but almost insoluble in ether. It is best recrystallized from hot water, in which it is quite soluble.

Hydrochloride of Ethyl Isourea (*Ethyl Imidocarbamate Hydrochloride*, $NH_2C(:NH)OC_2H_5.HCl$.—Eight and nine-tenths grams (1 mol.) cyanamide were dissolved in 275 grams (30 mol.) absolute alcohol, which had been freed from water by distillation over sodium; into this solution there were passed 9.3 grams (1.25 mol.) dry hydrogen chloride, the flask and contents being kept cold by ice during the absorption of the gas. After four days the solution no longer gave a test for cyanamide with ammoniacal silver nitrate. The greater portion of the solvent was distilled off at reduced pressure, the temperature not rising above 35°, and the solution then evaporated *in vacuo* over sulphuric acid and solid caustic potash. When near dryness the mother-liquor was separated from the crystals which had formed. The crystals thus obtained were transparent, rhombic plates, which, if pure, gave a neutral solution when dissolved in water. Analysis of these neutral crystals showed that they were ethylisourea monohydrochloride (Analysis I). Generally the salt was not so pure and required recrystallization before analysis. Unlike the hydrochloride of the methyl ether it could not be readily crystallized from alcohol, owing to its greater solubility in that solvent. But on treating the alcohol solution fractionally with ether the hydrochloride was precipitated. It showed at first a somewhat high percentage of chlorine (28.94 per cent), but after remaining for some time (ten days) in a vacuum over solid caustic potash, it gave a neutral reaction and analysis showed it to be pure (II). Allowed to remain in a vacuum over caustic potash for a longer period, it showed no further change in

[1] Weith: Ber. d. chem. Ges., 10, 1744.

composition (III and IV). In the analysis for nitrogen the combustion was carried out very slowly in order to prevent ethylene from passing over unburned and giving too high a percentage of nitrogen.

I. 0.2561 gram substance required 20.54 cc. tenth-normal $AgNO_3$.

II. 0.1638 gram substance required 13.18 cc. tenth-normal $AgNO_3$.

III. 0.1339 gram substance required 10.75 cc. tenth-normal $AgNO_3$.

IV. 0.1016 gram substance gave 19.7 cc. moist nitrogen at 16°.5 and 761 mm.

	Calculated for $NH_2.C(:NH).OC_2H_5.HCl$.	Found. I.	II.	III.	IV.
Cl	28.45	28.43	28.52	28.47	....
N	22.53	....	....	....	22.68

The hydrochloride of ethylisourea melts at 123° to 124° with evolution of ethyl chloride.

Ethylisourea Chlorplatinate, $(NH_2.COC_2H_5:NH)_2H_2PtCl_6$.—Solutions of ethylisourea hydrochloride and chlorplatinic acid in absolute alcohol were cooled to —10° and mixed. Scratching with a glass rod caused the chlorplatinate to be partially precipitated. Absolute ether was added to complete the precipitation.

The crystals are at first translucent, four-sided, dark-yellow plates, which after a few minutes become of a lighter color and opaque, as if a loss of alcohol of crystallization had occurred.

This change in the appearance of the crystals can be very readily followed under the microscope. The chlorplatinate tends to come out as an oil, unless the solution from which it is precipitated is quite cold. Analysis of three different preparations gave the following figures:

I. 0.0887 gram substance gave 0.0298 gram platinum.

II. 0.1522 gram substance gave 0.0505 gram platinum.

III. 0.1361 gram substance gave 0.0454 gram platinum.

	Calculated for $(NH_2.COC_2H_5:NH)_2H_2PtCl_6$.	Found. I.	II.	III.
Pt	33.25	33.60	33.18	33.36

The chlorplatinate is soluble in water, alcohol, and chloroform, but insoluble in ether. Heated in a melting-point tube it melts with decomposition at 178°.5.

Ethylisourea (*Imido Ethylcarbamate*),[1] $NH_2C(:NH)OC_2H_5$. —The free ethylisourea was obtained from the hydrochloride by the same method as was used in the preparation of methylisourea.

Ethylisourea is more soluble in ether than the methyl compound, and readily forms supersaturated solutions in that solvent, so that severe cooling and vigorous scratching with a glass rod are sometimes necessary to start the crystallization from the solution from which most of the ether has previously been distilled off. The yield is satisfactory, but not quantitative as in the case of the methyl compound.

The base was titrated against tenth-normal hydrochloric acid, using methyl orange as the indicator.

0.1551 gram substance required 17.52 cc. tenth-normal HCl; calculated 17.59 cc.

0.1702 gram substance required 19.18 cc. tenth-normal HCl; calculated, 19.30 cc.

0.2839 gram substance gave 0.4249 gram CO_2 and 0.2290 gram H_2O.

	Calculated for $C_3H_8N_2O$.	Found.
C	40.83	40.82
H	9.17	9.04

Ethylisourea distils *in vacuo* at 89° under a pressure of 10.5 mm., and at 95° to 96° at 15 mm. Some of the pure solid kept in a closely-stoppered bottle six weeks was found to have partially liquefied. Lack of time prevented the determination of the decomposition-products.

Ethylisourea is a strong base, its aqueous solution reacting strongly alkaline. Such a solution added to a solution of copper sulphate precipitates copper hydroxide. If an excess of the isourea ether is added the hydroxide redissolves, forming a purplish-blue solution. Ethylisourea, added to a solution of aluminium sulphate, first precipitates the hydroxide,

[1] Other names are ethoxyformamidine and ethyl imidoamidoformate.

but an excess of the isourea redissolves the precipitate. Parallel test-tube experiments with aluminium sulphate and equivalent amounts of ethylisourea and ammonia gave results showing that ethylisourea is a considerably stronger base than ammonia.[1] As one might expect from the general similarity to ammonia, an aqueous solution of ethylisourea dissolves silver chloride.

Action of Dilute Hydrochloric Acid on Ethylisourea.

An experiment carried out with ethylisourea parallel to that with methylisourea and hydrochloric acid[2] gave the analogous decomposition-products; ethyl chloride, urea, and a small amount of ethylurethane, $NH_2COOC_2H_5$. The amount of urethane found was slightly more than 1 per cent of the theoretically possible amount; without recrystallization it melted at 44° to 45°, and when it was mixed with Kahlbaum's synthetic ethylurethane (melting-point 49° to 50°) the melting-point was raised to 46° to 47°. The iodoform reaction failed to show the presence of ethyl alcohol.

Ethyl Phenylisobiuret (*Ethyl Phenylureidoimidoformate*), $C_6H_5NH.CO.NH.COC_2H_5 : NH$, was prepared in the same manner as the methyl phenylisobiuret, except that it was found better to recrystallize it by adding water to its solution in a small volume of methyl alcohol. Thus precipitated, the compound gives monoclinic prisms melting at 85°.5 to 86°. The yield was good.

The Hydrochloride of Ethyl Phenylisobiuret, $C_6H_5NHCONH.COC_2H_5 : NH.HCl$, was prepared by treating the ethyl ether with dry hydrogen chloride in ether solution. It melts with decomposition at 141°.

Analysis of the hydrochloride was made by dissolving it in dilute alcohol, adding alkali to neutrality (the salt was strongly hydrolyzed), and titrating with silver nitrate and chromate indicator.

0.3319 gram substance required 13.51 cc. tenth-normal $AgNO_3$.

[1] Quantitative determinations of the strength of the various classes of isoureaethers and imidoethers will be made. J. STIEGLITZ.

[2] See page 249.

	Calculated for $C_{10}H_{14}N_2O_2Cl$.	Found.
Cl	14.55	14.43

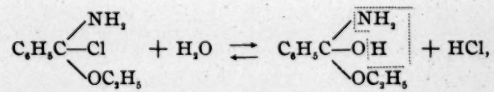
Action of Dilute Hydrochloric Acid on Ethyl Phenylisobiuret.

Ethyl phenylisobiuret was heated at 100° for three and a half hours with normal hydrochloric acid. The tube opened with pressure due to ethyl chloride. The solid was recrystallized from hot water and identified as phenylbiuret[1] by its melting-point and solubilities.

No ethyl alcohol could be detected in the filtrate by the iodoform reaction. That saponification of a part of the biuret had occurred, giving rise to aniline and ammonia, was shown by the filtrate giving with caustic potash an alkaline gas, and with chloroform and caustic potash a strong isonitril odor.

III. The Hydrolysis of the Hydrochloride of Ethyl Imidobenzoate and of the Hydrochloride of Ethyl Phenylisourea.

The difference in behavior towards water[2] of the hydrochlorides of the imidoethers, RC(: NH)OR, and the hydrochlorides of the urea ethers, RNHC(: NH)OR, forms one of the most interesting problems for investigation in this series of compounds, as the solution of this problem must have an important bearing on the determination of the constitution of the salts of imidoethers, etc.,[3] and on the whole subject of ester saponification.[4] The difference at the first glance[3] seems to be due to the difference in the strength of the imidoethers and urea ethers as bases: the salts of the weaker bases, the imidoethers, suffer hydrolysis to some extent, according to



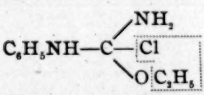
and give the decomposition-products of the hydrolyzed substance, *viz.*, ammonia and ethyl benzoate, the chlorides of

[1] Page 254.
[2] Page 210.
[3] Stieglitz: This JOURNAL, **21**, 101.
[4] *Ibid.*; Ber. d. chem. Ges., **32**, 1494.

these imidoethers being stable at ordinary temperatures. If the salts of the stronger bases, the urea ethers,

$$C_6H_5NHC(:NH)OR,$$

are not hydrolyzed, no decomposition would occur at ordinary temperatures, the chlorides being stable. And when decomposition is effected at higher temperatures in aqueous solution alkyl chloride and a urea would result, the decomposition-products of the salt



$$\rightarrow C_6H_5NHCONH_2 + ClC_2H_5.$$

These considerations would give us a simple and rational explanation of the difference in behavior of the two series of salts. In confirmation of this view it was shown qualitatively that imidoether salts dissolve in water with an acid reaction,[1] the urea ether salts $C_6H_5NH.C(:NH)OC_2H_5.HCl$ and $NH_2C(:NH)OC_2H_5.HCl$, give solutions perfectly neutral to sensitive litmus paper.[1] It seemed of particular importance, however, to investigate the subject from a quantitative point of view. A series of experiments has been completed by Mr. Wm. McCracken under the direction of Professor Stieglitz,[2] showing the close connection between the velocity of decomposition or saponification of two or three imidoethers and their strength as bases—ethyl imidobenzoate, ethyl imido-*m*-nitrobenzoate, and ethyl imido-*m*-brombenzoate being used; and this work is now being continued by Mr. J. W. Shepherd. The determination of the affinity constants of the imido and urea ethers and of the conductivity of their salt solutions[4] will be included in this investigation.[5] As a preliminary quantitative study, I have undertaken to compare

[1] Stieglitz: This JOURNAL, 31, 106.

[2] This paper, pp. 217 and 210.

[3] See foot-note p. 209.

[4] To determine the extent of hydrolysis.

[5] A particular study will have to be made of the salts of acylated urea ethers, which readily give off hydrochloric acid on being dissolved in water and still give alkyl chlorides and acylated ureas as the final decomposition-products.

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the extent of the hydrolysis of a typical imidoether salt, the hydrochloride of ethyl imidobenzoate, $C_6H_5C(:NH)OC_2H_5.HCl$, with that of a typical urea ether salt, the hydrochloride of ethyl phenylisourea, $C_6H_5NHC(:NH)OC_2H_5.HCl$, byt itrating the free acid formed according to the equation

$$C_6H_5C(NH_2)(OC_2H_5)Cl + H_2O \rightleftarrows C_6H_5C(NH_2)(OC_2H_5).OH + HCl.$$

This method, as is well known, does not show the absolutely correct degree of hydrolysis: with the salts of very weak bases, in fact, it cannot be used at all, since the hydrolysis continues long after the originally free acid is neutralized, until nearly all of the salt is decomposed.[1] However, with salts of tolerably strong bases and an indicator, methyl orange, which is very sensitive to hydroxyl ions, the method does give results sufficiently reliable for preliminary purposes of comparison. This follows from the fact that neutral solutions result when even very small amounts of alkali (two or three drops of tenth-normal solution) are added to the salt solution. It also follows from these considerations: hydrolysis is caused according to the above equation primarily because the dissociation constant of the base is smaller than that of hydrochloric acid. For

$$C_6H_5C(NH_2)OH(OC_2H_5) \rightleftarrows C_6H_5C(\overset{+}{O}C_2H_5)NH_2 + \overset{-}{O}H,$$

$$\frac{P \times OH}{m} = k',$$

where P, OH, and m denote respectively the concentrations of the positive imidoether ions, the hydroxyl ions, and the undissociated molecules, and k' the ionization constant.

Where k' is very much smaller than the ionization constant for hydrochloric acid, m must always be in very large excess over OH, and, as the neutralization of the hydrogen ions of the acid proceeds, the new hydroxyl ions produced from water will continue to form large quantities of the undissociated base m, releasing an equivalent number of new hydrogen ions. But when k' approaches the constant for hydrochloric acid,

[1] J. Walker: Ztschr. phys. Chem., 4, 319.

this is, of course, not the case; with the formation of a moderately small additional amount of the molecular base m, k' can be fulfilled and the solution become alkaline very easily. When k' equals k_{HCl}, as for sodium hydroxide, the first drop of alkali produces alkalinity, as in the case of sodium chloride.

The following results are to be considered, therefore, only as close approximations to the determination of the true degree of hydrolysis,[1] but they fulfil the purpose for which this preliminary study was undertaken. The results show plainly:

1. That the hydrochloride of ethyl imidobenzoate is hydrolyzed by water, and that the amount of hydrolysis in the concentration used (approximately twelfth-normal) is somewhat less than 1 per cent of the total salt.

2. That the hydrochloride of ethyl (and methyl) phenylisourea is not hydrolyzed at all (concentration approximately twelfth-normal).

3. That ethyl imidobenzoate must be a fairly strong base ionizing quite easily, and that the hydroxide

$$C_6H_5C(OC_2H_5)(NH_2)OH$$

(ionized), must form readily, more readily, for instance, than $C_6H_5NH_2OH$ (ionized).

4. That ethyl phenylisourea is a still stronger base, whose affinity constant will most likely be found to be close to that of potassium or sodium hydroxide.

The determinations were made by dissolving a known weight of the free ethers[2] in an excess of carefully standardized tenth-normal acid and titrating back the excess of acid with tenth-normal sodium hydroxide, the final concentration of the salt solutions being about one-twelfth normal. In the first determinations (1 to 4 and 9 to 14) the weighings and titrations were made in a large glass-stoppered weighing-bottle. Later it was found better to make the weighings in glass bulbs in order to avoid loss by evaporation, and to use a wide-

[1] More accurate results are expected from the determinations of the conductivity of the salt solutions. The calculation of the constants for hydrolysis has been postponed until the completion of these determinations.

[2] The free benzimidoether was prepared according to Bushong (this JOURNAL, 18, 490).

mouthed bottle for the titrations, the bulbs being broken by pressing with a heavy glass rod. In all the titrations methyl orange was the indicator used to determine the neutrality-point. The temperature was that of the laboratory, the determinations being made parallel to each other, at the same time. As a measure of precaution, the ethyl phenylisourea was distilled *in vacuo* just before using it. This seems not to have been necessary, for practically the same results were obtained from some of the ether which had stood in a desiccator for nearly a month.

In titrations 13 to 18 the ethyl imidobenzoate had stood for some days in a desiccator; for titrations 19 to 21 it was freshly distilled, that boiling at 106°.5 to 107° at 15.5 mm. being taken. In order to be more certain of its purity it was analyzed.

0.2787 gram substance gave 0.7376 gram CO_2 and 0.1899 gram H_2O.

	Calculated for $C_9H_{11}NO$.	Found.
C	72.41	72.18
H	7.45	7.64

Several determinations were also made with methyl phenylisourea (titrations 9 to 12).

A drop of tenth-normal acid makes a difference of about 0.2 per cent; the error of weighing is about a fourth as much.

The average amount of hydrolysis found for ethyl phenylisourea was 0.13 per cent (titrations 1 to 8); for the methyl ether 0.058 per cent (titrations 9 to 12). Both of these results are within the limit of error of the experiment and indicate that most likely no hydrolysis occurs with these isourea ethers.

In the case of ethyl imidobenzoate, omitting titration 20, which is obviously out of harmony with the others, the average found was 0.925 per cent. Mr. McCracken,[1] using a somewhat different method, found approximately 2 per cent hydrolysis in one-twentieth normal dilution and 1.3 per cent in one-fifth normal solutions.

In conformity with these results I found that the hydro-

[1] Pages 209 and 260.

chlorides of methyl[1] and ethyl[2] phenylisourea dissolve in water, giving solutions perfectly neutral to sensitive litmus.

Ethyl imidobenzoate hydrochloride gives an acid solution,[3] as is well known.

Ethyl Phenylisourea.

	Grams substance taken.	Calculated No. cc. N/10 HCl.	Found No. cc. N/10 HCl.	Final No. cc. solv'nt.	Percentage hydrolysis.
1	0.3884	23.654	23.583	26	0.30
2	0.4151	25.280	25.167	28	0.45
3	0.4253	25.901	25.875	31	0.10
4	0.4534	27.612	27.587	31	0.09
5	0.3231	19.677	19.671	22.5	0.03
6	0.2793	17.009	17.006	19	0.02
7	0.5087	30.980	30.904	34	0.24
8	0.3763	22.917	22.961	26.5	—0.19
				Average,	0.13

Methyl Phenylisourea.

9	0.4156	27.670	27.712	29	—0.15
10	0.4984	33.187	33.070	35	0.32
11	0.2722	18.112	18.123	20	—0.06
12	0.3653	24.324	24.293	27	0.13
				Average,	0.058

Ethyl Imidobenzoate.

13	0.2724	18.263	18.066	19.5	1.08
14	0.2801	18.779	18.582	20	1.05
15	0.4076	27.328	27.001	33	1.20
16	0.3901	26.154	25.948	33	0.79
17	0.3515	23.567	23.437	27	0.98
18	0.2986	20.020	19.840	23.5	0.90
19	0.3633	24.365	24.185	26	0.74
[20	0.3256	21.834	21.425	25	1.87]
21	0.5052	33.872	33.648	35.5	0.66
				Omitting [20], average,	0.925

The above investigations were carried out under the direction of Dr. Julius Stieglitz, and I wish to express here my sincere thanks for the personal interest he took in the work and the thoughtfulness with which he guided it.

[1] Page 229.
[2] Page 217.
[3] Stieglitz: This JOURNAL, 21, 106.

Contributions from the Sheffield Laboratory of Yale University.

LXXX.—ON THE PURIFICATION OF CAESIUM MATERIAL.

By H. L. Wells.

Several years ago[1] I recommended the use of the yellow salt $2CsCl.PbCl_4$ as a means of precipitating caesium from its solutions. Subsequent experience has shown that the method is very convenient for removing small quantities of the rare metal from all sorts of solutions; particularly from those from which the greater part of it has been precipitated by other means. For large quantities of caesium, however, the lead tetrachloride method, used alone, is inconvenient on account of the large amount of chloride that must be used, and because it is possible to obtain only very dilute solutions of lead chloride or of the white double salt, $CsCl.2PbCl_2$.[2]

I have used extensively the salt just mentioned as a means of precipitating caesium from concentrated solutions of the crude extract of pullucite, made by means of hydrochloric acid. The precipitation is made by adding a hot concentrated solution of the calculated amount of lead nitrate. The precipitate is crystalline and can be readily washed with dilute hydrochloric acid; then it can be very easily decomposed by boiling with ammonium carbonate solution. The method is satisfactory in a case where very little potassium and practically no rubidium are present, for, although it does not give a good separation from these metals, the precipitation of caesium is nearly complete. The precipitate $CsCl.2PbCl_2$, however, is very heavy compared with the amount of caesium that it contains, and its decomposition with ammonium carbonate produces 4 molecules of ammonium chloride for 1 of caesium chloride. For these reasons the method has been abandoned in this laboratory in favor of the method of Godeffroy.

In precipitating caesium according to Godeffroy's method I am accustomed to use less concentrated hydrochloric acid solutions than those that have been recommended. About

[1] Am. J. Sci., (3), **46**, 186.
[2] *Ibid.*, (3), **45**, 121.

one-third or one-half of the total volume of concentrated hydrochloric acid answers very well, and a solution of this kind possesses the advantage that it can be filtered by means of paper. To such a solution antimony trichloride, also dissolved in hydrochloric acid, is added as long as a precipitate forms. The latter is collected, best on a Büchner filter, and well washed with cold dilute hydrochloric acid.

To the filtrate and washings from the antimony salt, without concentrating them, lead nitrate is added at the rate of 2 or 3 grams per liter. This salt should be dissolved in water before it is added. Chlorine gas is then passed in until the solution is saturated with it. After standing for a few hours the liquid is decanted from the precipitate of the salt Cs_2PbCl_6 (which is usually colored green from the presence in it of the dark-blue salt Cs_2SbCl_6),[1] and is tested by the addition of a little more lead nitrate, and chlorine also if necessary. This precipitation is so complete, as far as caesium is concerned, that the liquid may be finally discarded. A liter of such a liquid will probably hold in solution only about 0.1 gram of the salt Cs_2PbCl_6, but the rubidium salt is nearly one hundred times more soluble. The lead tetrachloride salt should be washed on a Büchner funnel with cold dilute hydrochloric acid.

Formerly I was accustomed to decompose the antimony salt, $3CsCl.2SbCl_3$,[2] by suspending it in water and passing in hydrogen sulphide gas, but for large quantities this is a very slow and laborious operation, and it is much more convenient to treat it in a large porcelain dish with boiling dilute ammonium hydroxide. The antimonious oxide thus produced is dense and easy to filter and wash; moreover, it may be readily dissolved in hydrochloric acid and used again for precipitating caesium. A little antimony goes into solution in the ammonia, but this is readily removed, best after the liquid has become slightly acid by evaporation, by passing in hydrogen sulphide and filtering.

[1] Concerning this compound see the next article.

[2] The composition of this compound was very incorrectly determined by Godefroy, who gave it the formula $6CsCl.SbCl_3$. Setterberg first arrived at the correct formula, which was afterwards confirmed by Remsen and Saunders, and also by Muthmann, and by Wells and Foote.

The removal of ammonium chloride on a large scale by ignition is a very slow operation. It is therefore best, in most cases, after the hydrogen sulphide has been removed by evaporation, to add to the concentrated solution of caesium and ammonium chlorides, in a large porcelain dish, a liberal amount of concentrated nitric acid and to heat cautiously until frothing has ceased. When further additions of strong nitric acid produce no change of color nor evolution of gas upon heating, the ammonium salts are entirely destroyed and the caesium chloride changed to nitrate.[1] The solution of caesium nitrate in nitric acid is then evaporated to dryness, and the residue is heated until the acid nitrate[2] is decomposed and the normal nitrate is more or less completely fused. The evaporation of the nitrate to dryness in the presence of nitric acid over a free flame in a dish is not a difficult operation, since decrepitation takes place to a much less extent than is the case when the chloride is evaporated in the same way. A large mass of fused caesium nitrate should not be allowed to solidify quietly in the bottom of a porcelain dish, for on cooling it is liable to break the dish by its contraction. If it is stirred as it solidifies this danger is avoided.

Caesium nitrate is one of the most beautiful of salts for recrystallization. Like potassium nitrate, it is much more soluble in hot water than in cold, and it crystallizes upon slowly cooling a hot concentrated solution in the form of large, colorless prisms. I have found that recrystallizing this salt tends to purify it from traces of rubidium, for a large quantity of the salt which showed no rubidium spectrum, upon systematic recrystallization, showed a distinct spectrum for that metal in the final mother-liquor. This, however, is a slow method of purification if it is desired to carry the latter to the last degree, but the nitrate obtained by one or two recrystallizations is pure enough for any ordinary purpose, unless the original antimony salt was contaminated to an unusual extent.

[1] This method of destroying ammonium chloride is due to J. Lawrence Smith. See Am. J. Sci., (2), 34, 367.

[2] A description of the acid caesium nitrates will soon be published from this laboratory.

The nitrate is readily converted into carbonate by mixing it with 2 parts of pure oxalic acid, adding a little water, evaporating to dryness, and fusing the residue in a platinum crucible.[1]

Where the highest degree of purity in a caesium salt is desired, the salt $CsCl_3I$,[2] by its recrystallization, probably offers one of the best means for accomplishing that object. It is very much less soluble than the corresponding rubidium, potassium, sodium, and lithium salts. I have found that this salt may be made very conveniently from the nitrate by dissolving one part of the latter together with one atomic proportion of iodine in about 10 parts of 1 : 1 hydrochloric acid at a temperature just below boiling. The solution takes place quickly, and, upon cooling, the beautiful yellow salt crystallizes out. It is recrystallized by solution in hot 1 : 1 hydrochloric acid and cooling. One or two recrystallizations, when each crop is well drained and washed with a little cold dilute hydrochloric acid, give, even from impure materials, a remarkably fine product. From this trihalide by ignition, best at a very gentle heat so that the mass does not fuse, pure caesium chloride may be prepared.

APRIL, 1901.

LXXXI.—ON A SALT OF QUADRIVALENT ANTIMONY.

BY H. L. WELLS AND F. J. METZGER.

While engaged in purifying some caesium material we precipitated a large quantity of the salt $Cs_5Sb_2Cl_9$ by adding an excess of antimony trichloride to a hydrochloric acid solution of impure caesium chloride. A small amount of caesium remained in the filtrate, and, wishing to recover this, we added a solution of lead nitrate and passed chlorine gas into the liquid in order to precipitate the very insoluble lead tetrachloride salt, Cs_2PbCl_6.[3] Much to our surprise the precipitate, while showing the usual octahedral form, was bright-

[1] Method of J. Lawrence Smith, *Loc. cit.*
[2] Am. J. Sci., (3), **43**, 17.
[3] *Ibid.*, (3), **46**, 180.

green in color, whereas the pure lead salt is bright-yellow. The product was found to contain a small quantity of antimony, and by preparing the lead salt after the addition of varying quantities of antimony trichloride we obtained products of various colors, from yellowish-green to dark bluish-green. The following determinations were made in a lighter and a darker product :

	Light-green. Per cent.	Dark-green. Per cent.
Sb	0.92	1.44

These results indicated that antimony was not an essential constituent of the compound, and it seemed probable that some salt of antimony isomorphous with the salt Cs_2PbCl_6 had crystallized with it. We drew the further inference that the isomorphous antimony compound must be strongly colored, probably blue. Fortunately we had access to the reprint of an article by Setterberg[1] (which, as far as we can find, has not been noticed in any of the books of reference), where a peculiar black caesium-antimony salt is described. Setterberg made this compound by boiling a solution of antimony trichloride in strong hydrochloric acid with antimony pentachloride and caesium chloride in excess. He ascribes to it the formula $2CsCl.SbCl_4$ or $4CsCl.SbCl_3.SbCl_5$, and states that it forms black, very small, short prisms. It was evident that a salt of this composition might be expected to crystallize with one of the composition $2CsCl.PbCl_4$, and if so the fact would be a strong argument in favor of Setterberg's first formula, but his description of the form of the salt gave no evidence of the isomorphism of the two compounds.

We have prepared Setterberg's salt under varying conditions, and have confirmed his formula, as is shown by the following analysis of a very pure product :

	Calculated for Cs_2SbCl_6.	Found.
Cs	44.41	44.92
Sb	20.03	20.23
Cl	35.56	35.13
	100.00	100.28

[1] Öfversigt K. Vetensk-Akad. Förhandl., 1882, 23.

As far as can be judged by careful microscopic examination this salt crystallizes in perfect octahedra. We could find no indication of a prismatic form corresponding to Setterberg's description, hence it is probable that his crystals were so small that he did not make them out clearly. No optical examination of the crystals could be made on account of their complete opacity. The color of the crystallized substance is absolutely black, but when a little of it is rubbed between the ground surfaces of a glass-stoppered bottle it shows a very strong, dark-blue color.

From the crystalline form and color of this curious salt there can be no doubt that it was the substance which gave the green color to our products of the salt Cs_2PbCl_6, and it seems certain that the two salts are isomorphous. The color of the antimony salt indicates that it is not a compound containing antimony trichloride and pentachloride, for the known caesium double salts with these chlorides, $3CsCl.2SbCl_3$ and $CsCl.SbCl_5$,[1] are colorless or nearly so.

We are convinced, therefore, that this black salt, Cs_2SbCl_6, is a member of the well-known group of octahedral double halides of quadrivalent elements, among which are K_2PtCl_6, Cs_2SnCl_6, Cs_2TeCl_6, Cs_2TeI_6, K_2PbCl_6, and Cs_2PbCl_6, and that it is a double salt of antimony tetrachloride, $SbCl_4$.

Judging from the color of the double salt, the tetrachloride, $SbCl_4$, must be black. This color would be entirely unexpected, since the chlorides $SbCl_3$ and $SbCl_5$ are colorless. We have tried in vain to get some evidence of the separate existence of a black chloride by making mixtures of the two known chlorides at low and high temperatures and by treating the salt Cs_2SbCl_6 with cold concentrated sulphuric acid.

The oxide of antimony, Sb_2O_4 or SbO_2, is usually regarded as a compound of Sb_2O_3 and Sb_2O_5. It is possible that this may be a true dioxide, but it would be expected that an oxide which corresponded to a black chloride would be black also, for, if there is a difference in color, oxides are usually darker than the corresponding chlorides.

We have prepared a jet-black double bromide by using a

[1] Setterberg: *Loc. cit.*

method exactly like that by means of which the black double chloride was made. Judging from analogy, this is probably the salt Cs_3SbBr_6, but we were unable to get a product that was pure enough for analysis, as it was always mixed with more or less light-colored impurity. We attempted, without success, to make the corresponding iodide and fluoride.

APRIL, 1901.

LXXXII.—ON THE ACID NITRATES.

BY H. L. WELLS AND F. J. METZGER.

A number of years ago it was noticed by one of us that when caesium nitrate is evaporated with strong nitric acid the last part of the acid is expelled with some difficulty, and the probable existence of a rather stable acid nitrate suggested itself. Mr. A. P. Beardsley, of this laboratory, undertook an examination of the matter last year, and upon dissolving caesium nitrate in hot nitric acid of sp. gr. 1.42 and cooling, obtained beautifully crystallized crops of the salt $HNO_3.CsNO_3$. The circumstances were such that Mr. Beardsley's work in this direction was interrupted, and we have undertaken a further examination of the subject.

Ditte[1] has described the following list of acid nitrates: $KNO_3.2HNO_3$, $NH_4NO_3.HNO_3$, $NH_4NO_3.2HNO_3$, [$2RbNO_3.5HNO_3$], [$TlNO_3.3HNO_3$].

The two formulæ enclosed in brackets do not correspond to the others or to the caesium salt mentioned above, and we have found that they are incorrect. In making these alleged compounds, $2RbNO_3.5HNO_3$ and $TlNO_3.3HNO_3$, Ditte saturated "monohydrated" nitric acid (the liquid corresponding to the formula HNO_3) with the normal nitrates and then simply analyzed the solution. He had prepared the other acid nitrates in the same way, but in these cases, having performed the operation above their melting-points, he was able to make definite compounds, and showed that the solutions became solid at definite temperatures.

We have easily succeeded in crystallizing two caesium and

[1] Ann. chim. phys., [5], 18, 320 (1878).

two rubidium acid nitrates, and a single thallium salt, and find that the salts of the last two metals do not correspond to the formulæ given by Ditte.

We have confirmed the composition of his potassium acid nitrate, and since his ammonium salts correspond exactly to the caesium and rubidium compounds, we assume that they are correct. Our revision and additions lead to the following list of acid nitrates:

	$KNO_3.2HNO_3$
$NH_4NO_3.HNO_3$	$NH_4NO_3.2HNO_3$
$RbNO_3.HNO_3$	$RbNO_3.2HNO_3$
$CsNO_3.HNO_3$	$CsNO_3.2HNO_3$
	$TlNO_3.2HNO_3$

These salts belong to two types, of which the diacid form is evidently most readily produced, since thallium and potassium apparently do not yield the other. The caesium salts are more easily prepared and are more stable than the others.

It has been supposed that "monobasic" acids are incapable of forming acid salts, and it is evident that this belief prevails at the present time, for the following statement is made in a recent text-book: "Acids like hydrochloric and nitric acids have not the power to form acid salts. They are called *monobasic acids*." This statement seems to be too sweeping, for there are many acid chlorides, some of which are well known and remarkably stable; in fact, their stability when in solution apparently leads to the opinion that they are not real acid salts. The following list will serve as examples of these compounds: $2HCl.PtCl_4$; $HCl.AuCl_3$; $2HCl.SnCl_4$; $HCl.ZnCl_2.2H_2O$; $2HCl.CuCl$; $2HCl.CuCl_2$; $5HCl.SbCl_3.10H_2O$. Iodides and bromides are also known, for example, $2HBr.SnBr_4$ and $HI.AgI$. The ease with which hydrofluoric acid forms acid salts is remarkable, and many acid salts of univalent organic acids, such as acetic, propionic, and valerianic acids are well known. Since it is now shown that the acid nitrates are well defined and in some cases comparatively stable bodies, the old idea that only "polybasic" acids are capable of forming acid salts should be entirely abandoned. The

circumstance that acid nitrates are not more numerous is doubtless connected with the fact that double nitrates in general are rare.

Method of Preparation.—The monoacid salts $RbNO_3.HNO_3$ and $CsNO_3.HNO_3$ are readily prepared by saturating nitric acid of sp. gr. 1.42 with the normal nitrates at a gentle heat and cooling to crystallization. The use of a freezing-mixture, such as ice and salt, is desirable in making the rubidium compound, but it is not necessary for the caesium salt. Only normal potassium nitrate and thallous nitrate could be crystallized from nitric acid of this strength.

The diacid salts $KNO_3.2HNO_3$, $RbNO_3.2HNO_3$, $CsNO_3.2HNO_3$, and $TlNO_3.2HNO_3$ were all prepared by dissolving the normal nitrates to saturation in nitric acid of sp. gr. 1.50, and cooling with a freezing-mixture usually to considerably below 0°. In preparing the thallous compound, warming must be avoided because it causes the oxidation of a part of the thallium to thallic nitrate. When this has happened we find that the addition of alcohol, after the removal of most of the strong nitric acid by evaporation, is a convenient means of converting thallic nitrate into the thallous salt.

Properties.—The monacid salts $RbNO_3.HNO_3$ and $CsNO_3.HNO_3$ form large, flat masses of small, colorless, transparent crystals, apparently octahedra, arranged in parallel position. The diacid salts $RbNO_3.2HNO_3$ and $TlNO_3.2HNO_3$ form beautiful, colorless, transparent needles, while $CsNO_3.2HNO_3$ forms large, thin, colorless, transparent plates.

All the acid nitrates give off nitric acid more or less rapidly upon exposure to the air at ordinary temperature. The salt $TlNO_3.2HNO_3$ must be dried on paper in a very cool place, as its melting-point is below the ordinary temperature. The salt $RbNO_3.2HNO_3$ decomposes rapidly, and this also must be prepared for analysis in a cool place. The salt $RbNO_3.HNO_3$ and the two caesium salts are more stable than the others; the monacid salts are almost stable in the air, and may be preserved indefinitely in hermetically sealed tubes.

The melting-points of the acid nitrates as given by Ditte and found by ourselves are as follows:

$NH_4NO_3.HNO_3$	9° (Ditte)
$RbNO_3.HNO_3$	62°
$CsNO_3.HNO_3$	100°
$KNO_3.2HNO_3$	—3° (Ditte)
$TlNO_3.2HNO_3$	Undetermined
$NH_4NO_3.2HNO_3$	18° (Ditte)
$RbNO_3.2HNO_3$	39° to 46°
$CsNO_3.2HNO_3$	32° to 36°

The melting-points of the rubidium and caesium monacid nitrates are sharp, but the corresponding diacid salts melt gradually, evidently on account of decomposition. The salt $TlNO_3.2HNO_3$ melts below the ordinary temperature, but its exact melting-point was not determined.

Analyses.—The acid nitrates are very easily analyzed. The amount of normal nitrate was determined by simple heating, and the amount of nitric acid by titration. The following analyses were made with separate crops of the different compounds:

Monacid Rubidium Nitrate, $HNO_3.RbNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	30.00	30.51	....	30.18
$RbNO_3$	70.00	....	70.43	....

Monacid Caesium Nitrate, $HNO_3.CsNO_3$.

	Calculated.	Found. I.	II.	III.	IV.[1]
HNO_3	24.42	24.23	24.13	....	24.28
$CsNO_3$	75.58	....	....	76.48	75.52

Diacid Rubidium Nitrate, $2HNO_3.RbNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	46.15	45.79	....	....
$RbNO_3$	53.85	....	53.74	53.44

Diacid Caesium Nitrate, $CsNO_3.2HNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	39.25	39.23	39.86	....
$CsNO_3$	60.75	....	....	61.22

[1] Determinations by H. P. Beardsley.

Diacid Thallous Nitrate, $TlNO_3.2HNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	32.14	33.13	33.02	....
$TlNO_3$	67.86	....	....	67.00

APRIL, 1901.

LXXXIII.—INVESTIGATIONS ON DOUBLE NITRATES.

I. CAESIUM DOUBLE NITRATES.

BY H. L. WELLS AND H. P. BEARDSLEY.

Comparatively few double nitrates have been described, and it is a curious circumstance that most of these are compounds of metals of the rare-earth group, as follows:

$2KNO_3.Ce(NO_3)_3.2H_2O$
$2NH_4NO_3.Ce(NO_3)_3.4H_2O$
$2NH_4NO_3.La(NO_3)_3.4H_2O$
$2NH_4NO_3.Di(NO_3)_3.4H_2O$
$3Mg(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Zn(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Mn(NO_3)_2.2Ce(HO_3)_3.24H_2O$
$3Co(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Ni(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Mg(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Zn(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Mn(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Ni(NO_3)_2.2La(NO_3)_3.36H_2O$
$3Zn(NO_3)_2.2Di(NO_3)_3.60H_2O$
$3Ni(NO_3)_2.2Di(NO_3)_3.36H_2O$
$3Co(NO_3)_2.2Di(NO_3)_3.48H_2O$
$2KNO_3.Ce(NO_3)_4.1\frac{1}{2}H_2O$
$2NH_4NO_3.Ce(NO_3)_4.1\frac{1}{2}H_2O$

In addition to the above, the only normal double nitrates that have been found mentioned in the literature are the following:[1]

[1] There are known, however, certain easily fusible mixtures of nitrates, such as potassium and lead nitrates, and thallous and silver nitrates, but apparently these do not form definite, crystallized compounds.

$KNO_3.Au(NO_3)_3$
$2KNO_3.Tl(NO_3)_3.H_2O$
$2NH_4NO_3.HgNO_3.2\frac{1}{2}H_2O$
$NH_4NO_3.AgNO_3$
$KNO_3.AgNO_3$
$3KNO_3.AgNO_3(?)$

With the exception of the auric and thallic salts, these are all compounds of an alkaline nitrate with a univalent nitrate. It appears to be a singular fact that no double nitrates of alkaline and bivalent metals are known to exist.

Since caesium is known to form double salts with great facility, we have attempted to prepare double nitrates of this metal with several bivalent metals which generally form double salts very readily. For this purpose we selected lead nitrate, cobalt nitrate, and mercuric nitrate; but after the most careful work we were unable in any case to obtain a definite crystallized product, except crops of the simple nitrates. In each case there was evidence of combination from the fact that solutions were obtained which were much too concentrated to hold in solution the caesium nitrate that was present, if it had been uncombined. We conclude, therefore, that double nitrates were formed in solution in these cases, but that they were so exceedingly soluble that they could not be crystallized.

It seemed desirable to determine whether trivalent nitrates, other than those of the rare-earth metals, are capable of forming double nitrates with caesium nitrate. For this purpose we selected ferric nitrate, and succeeded, although with some difficulty, in preparing a double nitrate.

Caesium Ferric Nitrate,
$CsNO_3.Fe(NO_3)_3.7H_2O$.

This salt is formed at a rather low temperature in very concentrated solutions containing nitric acid and nearly equal molecular proportions of the compound salts. It forms pale-yellow, deliquescent, prismatic crystals, which melt, not sharply, at 33° to 36°. The following analyses were made with separate crops:

	Calculated for $CsNO_3.Fe(NO_3)_3.7H_2O$.	Found. I.	II.	III.
$CsNO_3$	34.64	....	35.51	34.87
$Fe(NO_3)_3$	42.98	42.29	42.73	42.68
H_2O	22.38	....	....	22.92
N	9.94	....	....	9.54

2. CAESIUM BISMUTH NITRATE, $2Cs_3NO.Bi(NO_3)_3$.

By G. S. Jamieson.

As a continuation of the investigation just described, experiments have been conducted with caesium nitrate and bismuth nitrate. The two salts were dissolved in widely varying proportions in dilute nitric acid, and the solutions were evaporated until crystallization took place on cooling. When 2.5 or more molecules of caesium nitrate to 1 molecule of bismuth nitrate were present, the simple caesium salt crystallized out; on the other hand, when the ratio of caesium to bismuth was less than about 1.5 to 1, bismuth nitrate was obtained. Between these limits a double salt was produced, particularly upon agitating the cold solution, in the form of colorless, prismatic crystals, which are stable upon exposure. These were sometimes more than a centimeter in length. The salt melts at 102°. Two crops gave the following analyses:

	Calculated for $2CsNO_3.Bi(NO_3)_3$.	Found. I.	II.
$CsNO_3$	49.75	47.00	51.22
$Bi(NO_3)_3$	50.25	52.63	48.16

The analyses do not agree very satisfactorily with each other, or with the calculated numbers. This was doubtless due to the syrupy nature of the mother-liquors, which made the drying of the crystals by means of filter-paper a difficult matter. The appearance of the crystals, in being homogeneous and different from the separate nitrates, however, leaves no doubt that this is a definite double nitrate.

3. THALLOUS THALLIC NITRATE, $2TlNO_3.Tl(NO_3)_3$.

By F. J. Metzger.

When thallous nitrate is dissolved in concentrated nitric acid (sp. gr. 1.50) by the aid of heat, a part of the salt is

oxidized to thallic nitrate, and upon cooling the properly concentrated solution, large, colorless, transparent, prismatic crystals are formed. The salt is very stable in dry air, but blackens when exposed to moisture. It melts at 150°. Several crops, made under different conditions, were analyzed.

	Calculated for $2TlNO_3.Tl(NO_3)_3$.	Found. I.	II.	III.
$Tl(NO_3)_3$	42.30	43.12	43.13	....
Total Tl	66.37	65.30	65.53	65.30

The thallic nitrate was determined by titrating the iodine set free by the salt from potassium iodide solution. The total thallium was weighed as iodide.

Conclusions.—No evidence has been obtained that alkaline nitrates form crystallizable double nitrates with the nitrates of bivalent metals.

Several trivalent nitrates, other than those of the rare-earth metals, are capable of forming double nitrates.

APRIL, 1901.

LXXXIV.—ON CAESIUM PERIODATE AND IODATE-PERIODATE.

BY H. L. WELLS.

The two salts to be described were obtained as the result of an attempt to make a thorough investigation of the caesium salts of periodic acid. In view of the well-known complexity of periodates in general, it was expected that a considerable number of caesium periodates would be found, and it was hoped that they might be of much theoretical interest. As a result, however, only normal caesium periodate, $CsIO_4$, was obtained when caesium carbonate was added in widely varying proportions to solutions of periodic acid. This was so disappointing that experiments upon the addition of periodic acid to caesium hydroxide solutions, which were originally planned, were not carried out.

Preparation of Periodic Acid.—The principles involved in the method used for this purpose are not new, but as some of the details may be of use to others, a brief description of the process is given: 12.7 grams of iodine are put into a 10 per cent

solution of 60 grams of sodium hydroxide. The liquid is heated to boiling in a flask, and a rapid stream of chlorine gas is passed into the continually boiling solution until the large amount of precipitate suddenly formed begins to cause bumping, when the flame is instantly removed, and the stream of chlorine is continued until no further increase is observed in the white precipitate of the periodate, $H_3Na_2IO_6$. While the liquid is still warm the precipitate is collected on a Büchner funnel and then thoroughly washed with cold water. It is dried in a steam-bath. The yield is usually about 22 grams, or 80 per cent of the theoretical. The sodium periodate is suspended in a large volume of water, 3 molecules of silver nitrate in solution are added, the liquid is boiled, filtered hot, and the black precipitate of silver periodate, Ag_3IO_5, is washed thoroughly with water.[1] The black silver periodate, while still moist, is suspended in a small amount of water, and chlorine gas[2] is passed in persistently, with agitation, until the precipitate has become nearly white. The silver chloride is removed by filtration, the liquid is concentrated on the water-bath, then brought to crystallization over sulphuric acid. After being drained the beautiful crystals of periodic acid are ready for use.

Caesium Periodate, $CsIO_4$.—This salt crystallizes in white plates, and is rather sparingly soluble in cold water. It was formed upon adding small quantities of caesium carbonate to concentrated solutions of periodic acid, and also when larger quantities, up to an excess of caesium carbonate, were used. It can be recrystallized readily by dissolving in hot water and cooling. When a very large excess of caesium carbonate was added to a solution of the salt and the mixture was evaporated to the point of crystallization more or less caesium iodate, $CsIO_3$, usually was formed on account of an accidental, or perhaps spontaneous, reduction, but no evidence of the exis-

[1] The filtrate contains a considerable amount of periodate which is kept in solution by the nitric acid set free by the reaction. Most of this may be recovered in the form of the golden-yellow salt $H_3Ag_2IO_6$ by evaporating the liquid to very small volume and cooling, or after evaporating to dryness on the water-bath another crop of Ag_3IO_5 may be obtained by treatment with water.

[2] According to my experience chlorine is much better than bromine for this purpose.

tence of any other periodate was thus obtained. The following analyses of six separate crops were made, most of them for the purpose of identification :

	Calculated for $CsIO_4$.	Found. I.	II.	III.	IV.	V.	VI.
Cs	41.05	42.02	40.37	....	....	....	....
I	39.20	....	38.19	....	....	....	....
O	19.75	19.62	19.77	19.61	19.45	19.65	19.20

Caesium was determined by treating the substance with concentrated sulphuric acid, evaporating, converting into normal sulphate by ignition in air containing ammonia, and weighing. Iodine was determined as silver iodide after reduction with sulphurous acid solution. Oxygen was determined by titrating with sodium thiosulphate the iodine set free by the substance in a solution of potassium iodide in the presence of an acid.

Acid Caesium Iodate-Periodate, $HCsIO_3IO_4.2H_2O$.—This curious salt was first noticed as having crystallized after spontaneous evaporation from a solution of caesium periodate in dilute periodic acid, in which the periodate had suffered partial reduction. A second crop was purposely prepared from a similar solution, and a third product was made by dissolving caesium iodate and periodate in dilute periodic acid and cooling. It forms beautiful, slender, white prisms. The three crops gave the following results upon analysis :

	Calculated for $HCsI_2O_7.2H_2O$.	Found. I.	II.	III.
H	0.19	....	....	....
Cs	24.80	....	24.00	....
I	47.39	....	47.38	47.11
O	20.90	20.75	20.58	....
H_2O	6.72	....	....	....
	100.00			
Iodine as I_2O_4	23.69	....	....	23.20
" " I_2O_7	23.69	....	....	23.91

Iodic acid was determined by dissolving the substance in dilute nitric acid, precipitating silver iodate by the addition of silver nitrate, and weighing the silver iodide resulting from

its ignition. The periodic acid left in the filtrate from the silver iodate was reduced by the addition of sulphurous acid, and the iodine was determined as silver iodide.

APRIL, 1901.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XIX.—CAMPHORIC ACID.

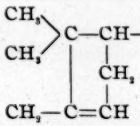
[TENTH PAPER.]

RACEMIC CAMPHOLYTIC ACID AND RACEMIC DIHYDROHYDROXYCAMPHOLYTIC ACID.

BY WILLIAM A. NOYES AND W. M. BLANCHARD.

A general concensus of opinion with regard to the structure of β-campholytic acid[1] appears to have been reached, and the work of Blanc, together with the synthesis of the 2-3,3-trimethylcyclopentanone effected in this laboratory, seem to place that structure beyond reasonable question.

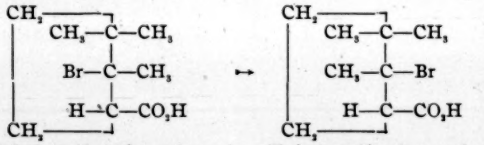
Several of the chemists referred to have also adopted Bredt's formula for camphoric acid, and the following formula for α-campholytic acid:



We will not now enter into a full discussion of this formula, but will remark, in passing, that the evidence for the formula rests chiefly on the oxidation-products of the acid. It seems possible that these oxidation-products are abnormal, just as the oxidation-products of the β-campholytic acid are known to

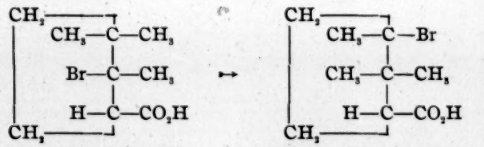
[1] Bredt, Lapworth, Blanc, Kerschbaum and Tigges, Walker, Perkin, and Forster have all expressed themselves, recently, as considering the acid to be $\Delta^{1}{}_{2}$,3,3-trimethylcyclopentenecarboxylic acid. We adopt for the acid the designation proposed by Kerschbaum and Tigges (Ber. d. chem. Ges., 33, 2936), as satisfactory. Forster's objection that the two campholytic acids are structurally different, even if it should prove that this is true, is not valid, since the α- and β-campholytic acids are, in any case, intimately connected, while there certainly is no close connection between β-campholytic acid and lauronolic acid. As Blanc and Bredt have also expressed themselves in favor of the nomenclature proposed, it is to be hoped that it may soon meet with general approval and that the name isolauronolic acid may be dropped.

be. The trans formula discussed in our last paper furnishes a better explanation of almost all other facts with regard to the acid. In that paper[1] the opinion was expressed that Walker's inactive campholytic acid was the racemic form corresponding to the α-campholytic acid. We have now secured evidence which establishes the correctness of this view. The acid required for the investigation was prepared by allowing β-campholytic acid to stand in contact with fuming hydrobromic acid for several days, and by decomposing the resulting hydrobromide with caustic potash or caustic soda. As Walker supposed,[2] but did not fully prove, the hydrobromide of the β-campholytic acid at first formed gradually passes over, almost completely, into the hydrobromide of the α-acid. If we adopt the trans formula for α-campholytic acid the change takes place thus :



Hydrobromide of β-campholytic acid. Hydrobromide of α-campholytic acid.

Such a transformation is in accord with the changes which are usual in stereomeric bodies and requires no special explanation. Bredt's formula, on the other hand, requires the following change :



Hydrobromide of β-campholytic acid. Hydrobromide of α-campholytic acid.

A transfer of the methyl group in the opposite direction

[1] This JOURNAL, 24, 286.

[2] J. Chem. Soc., 77, 378.

must, of course, be supposed in the conversion of α-campholytic acid and of dihydrohydroxycampholytic acid into β-campholytic acid. While such transformations find their analogy, as Blanc[1] has pointed out, in the transformation of pinacone to pinacoline and *vice versa*, the explanation seems less probable than that given by ourselves. It was shown in the last paper that the hydrobromide of the active α-campholytic acid has not only the structure but also the exact configuration corresponding to the dihydrohydroxycampholytic acid. The significance of this fact seems to have been overlooked by Bredt, Forster, and others in their discussion. The trans formula explains it satisfactorily[2] while no other formula thus far proposed does so.

When the hydrobromide of the racemic α-campholytic acid is treated with caustic soda there is formed, in addition to the regeneration of the campholytic acid, a small amount of the lactone first discovered by Kerschbaum and Tigges[3] and afterwards prepared by Blanc[4] and by Bredt,[5] and, in our experience, a small but, relatively, larger amount of a new hydroxy acid, which we have proved to be the racemic form of the well-known dihydrohydroxycampholytic acid, by separating it into its optically active components and identifying the right-handed form with that acid. As this new hydroxy acid undoubtedly corresponds in configuration to the hydrobromide of the racemic α-campholytic acid, and as that hydrobromide is always formed by the addition of hydrobromic acid to the racemic acid, it follows that that addition produces but *one* configuration (in a racemic form, of course) instead of the *two* configurations which an acid having Bredt's formula would give. The trans formula again gives a satisfactory explanation of these facts, while no other formula proposed does so.

The formation, in small amount, of a lactone on treating dihydroaminocampholytic acid with nitrous acid, leads Kersch-

[1] Compt. rend., 131, 803.
[2] This JOURNAL, 24, 289.
[3] Ber. d. chem. Ges., 33, 2938.
[4] Bull. soc. chim., 33, 81.
[5] Ann. Chem. (Liebig), 314, 392.

baum and Tigges, and Bredt to the conclusion that the amino group in that acid is in the γ position with regard to the carboxyl. This conclusion loses a part of its force from the following considerations: Camphoric acid, dihydroaminocampholytic acid, dihydrohydroxycampholytic acid, and the hydrobromide of α-campholytic acid are all active.

For camphoric acid	$[\alpha]_D = +47.2^\circ$
" dihydroaminocampholytic acid	$[\alpha]_D = +53.7^\circ$
" dihydrohydroxycampholytic acid	$[\alpha]_D = +72^\circ$
" bromdihydrocampholytic acid	$[\alpha]_D = +93^\circ$

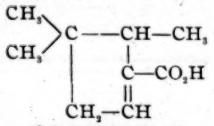
There is every reason to believe that these bodies all have the same configuration, differing only in the successive replacement of the carboxyl group by the amino group, by hydroxyl and by bromine. The new lactone, on the other hand, is inactive and must have, at least, a different configuration. That it is not derived from the racemic form of dihydrohydroxycampholytic acid is proved by the fact that the latter melts at 176° (see below), while the hydroxy acid corresponding to the lactone melts at 121°. That this acid is a stereomeric form, as suggested by Kerschbaum and Tigges, is possible, but cannot be considered as proved.

Bredt states recently in a foot-note[1] that the nitroso derivative of the anhydride of dihydroaminocampholytic acid gives the lactone on warming with sodium hydroxide. While it may be true that a small amount of the lactone is formed in this way, we find that the chief products of the decomposition are active α-campholytic acid and the active dihydrohydroxycampholytic acid. The last two products and *not* the lactone evidently correspond in structure to the amino acid. Further, we find that the active dihydrohydroxycampholytic acid is not converted into a lactone by acetic anhydride.

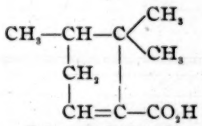
By the reduction of the hydroiodide of the racemic α-campholytic acid we have prepared a new dihydro-α-campholytic acid. From this we have obtained the α-bromine derivative, and from this, by means of alcoholic potash, a new campholytic acid. The double union in this acid must be in the position

[1] Ann. Chem. (Liebig), 314, 392.

Δ^3 whether we accept the Perkin-Bouveault or Bredt's formula for camphoric acid.



Δ^3-Campholytic acid. (Perkin-Bouveault.)



Δ^5-Campholytic acid. (Bredt.)

The latter of these formulae has been recently proposed for α-campholytic acid by Forster. As the new acid is different from either α-campholytic acid or Forster's infracampholenic acid neither of these acids can have the structure represented by the second formula. An acid of either formula could be separated into optically active forms, but stereomeric forms are, otherwise, impossible.

EXPERIMENTAL PART.

The racemic α-campholytic acid was prepared by the method of Walker and Cormack.[1] Twenty grams of β-campholytic acid were placed in a Drechsel wash-bottle, 40 cc. of hydrobromic acid added, and a slow stream of hydrobromic acid gas was passed into the mixture for several days. The hydrobromide was then dissolved in ligroin and the solution shaken with a 10 per cent solution of caustic soda, the ligroin being shaken alternately with the hydrobromide and with the caustic soda till all of the hydrobromide had dissolved. On acidifying the alkaline solution and adding ligroin, the campholytic acid dissolves, while a portion of the racemic hydroxy acid remains undissolved and can be separated at once. A portion of the hydroxy acid remains in the aqueous solution and can be extracted with ether. Approximately 15 per cent of the hydrobromide is converted into the hydroxy acid.

The Racemic α-Campholytic Acid, $C_8H_{13}CO_2H$, boils at 127° to 128° under a pressure of 14 mm. It has heretofore been described as an oil, but one especially pure specimen crystal-

[1] J. Chem. Soc., 77, 380.

lized in a cold room, and the crystals melted at 31°. An attempt to separate the acid into its components by means of the cinchonine and strychnine salts met with only a partial success, because of the unsatisfactory character of the salts. In one case an acid giving a slight rotation was obtained, but not in sufficient quantity or purity to determine the specific rotation.

The Racemic Dihydrohydroxy Campholytic Acid, $C_8H_{14}\begin{cases}CO_2H\\OH\end{cases}$, prepared as described above, crystallizes from acetic ether or from water in needles which melt at 176°. The acid is stable toward permanganate. When warmed with dilute sulphuric acid it is converted into β-campholytic acid, melting at 132°.

I. 0.2012 gram substance gave 0.4612 gram CO_2 and 0.1680 gram H_2O.

II. 0.1561 gram substance gave 0.3586 gram CO_2 and 0.1312 gram H_2O.

	Calculated for $C_9H_{16}O_3$.	Found. I.	II.
C	62.70	62.50	62.64
H	9.30	9.27	9.33

The hydroxy acid may also be prepared directly from the racemic α-campholytic acid by shaking it for a few minutes with fuming hydrobromic acid and treating the hydrobromide formed with caustic soda as before. This, together with the relation which was established in the last paper between the active α-campholytic acid, active hydroxy acid and active hydrobromide, leaves no doubt that the campholytic acid under discussion is in reality the racemic form corresponding to the active α-campholytic acid. That the hydrobromides of the active and racemic acids melt at the same temperature, is due to the fact that both melt with decomposition. The temperature of decomposition would be the same for an active as for the racemic form, while true melting-points are usually different, as is the case with the hydroxy acids.

Separation of the Racemic Dihydrohydroxycampholytic Acid into Its Components.

After several ineffectual attempts, the following method of

separating the racemic hydroxy acid was successful. Molecular equivalents of the acid and of strychnine were put into a flask with 100 cc. of water for each gram of strychnine, and the mixture was heated for twenty-four hours on a water-bath. The solution was then filtered and allowed to evaporate spontaneously. When the solution was reduced to about one-fifth of its original volume, a number of fine, needle-like crystals were obtained. On further evaporation a new crop of crystals was formed and the process was continued till the solution was carried to dryness. The hydroxy acid was recovered from the various portions of the salt, and that from the first two portions was found to consist of a mixture of the inactive acid with the dextro acid, while the later portions consisted of the inactive acid with the laevo acid. By fractional crystallization, the inactive acid was removed from each, and there were finally obtained two portions, each melting at 132°, and one right-handed, the other left-handed, in its action on polarized light. When the dextro acid was mixed with some of the dextro acid prepared from dihydroaminocampholytic[1] acid, the melting-point was not changed. But when a portion of the laevo acid was mixed with some of the dextro acid prepared from the amino acid, the melting-point rose to 176°. A mixture of the two acids obtained from the inactive hydroxy acid also melted at 176°. This melting-point test with mixtures, because it can be so easily applied to small quantities of the acids, was extremely useful in following the course of the separation.

Owing to the difficulties of the separation, the rotation was determined with small amounts of the acids and with portions which were not quite pure.

I. 0.0765 gram of the dextro acid in 10 cc. of water gave a rotation of +0°.87 in a tube 188.6 mm. long.

II. 0.0908 gram of the laevo acid in 10 cc. of water gave a rotation of —1°.1 in the same tube.

This gives for the dextro acid $[\alpha]_D = +62°.3$ and for the laevo acid $[\alpha]_D = -64°.3$. The value for the pure dextro acid is +72°.

In the work just described β-campholytic acid has, for the first time, been connected with an active derivative of cam-

[1] This JOURNAL, 17, 424.

phoric acid. The significance of the relation established has already been discussed.

Amide of the Racemic α^1-Campholytic Acid.—This was prepared by treating the acid successively with phosphorus pentachloride and ammonia. Blanc[1] gives the melting-point as 103°. We found it a little lower, but did not purify the amide very carefully. The amide was prepared for comparison with the amide of Forster's infracampholenic acid, a sample of which Professor Forster very kindly sent us. The two are different. The amide of infracampholenic acid crystallizes in needles, this amide in leaflets, and the melting-points differ by 13°. A mixture of the two amides melts at a lower temperature than either.

Racemic α-campholytic acid differs from infracampholenic acid, also, in its conduct toward bromine. The latter gives a tribromdihydroinfracampholenic acid,[2] while the campholytic acid gave us, under the same conditions, in a solution in carbon disulphide, a mixture of dibrom-α-campholytic acid melting at 109° and dibrom-β-campholytic acid melting at 141°. The former gave, on analysis, 51.33 per cent of bromine, the latter 51.13 per cent. Theory requires 50.95 per cent.

Racemic Dihydro-α-Campholytic Acid, $C_8H_{15}CO_2H$.—Many unsuccessful attempts have been made, in this laboratory, in the endeavor to reduce the α-campholytic acid. The inactive acid has finally been reduced as follows: The hydroiodide of *i*-α-campholytic acid was prepared by passing hydriodic acid into a solution of the acid in ligroin.[3] The hydroiodide was then dissolved in cold alcohol and reduced by means of zinc dust. After separating the acids which resulted, they were dissolved in a solution of sodium carbonate and a solution of potassium permanganate added as long as it was decolorized. Acid sodium sulphite and sulphuric acid were then added in excess and the new acid was distilled over with water vapor. The acid was then taken up with ether, dried, and analyzed. As the analysis indicated that the acid was not quite pure, what remained was distilled. It showed a small amount of

[1] Bull. soc. chim., **23**, 73.
[2] J. Chem. Soc. (London), **79**, 114.
[3] Blanc: Bull. soc. chim., **23**, 81.

iodine vapors, on distillation, and was, accordingly, boiled with zinc and dilute sulphuric acid and distilled once more with steam. After drying, the acid was analyzed again and gave correct results. (Analysis II, below.)

I. 0.1788 gram substance gave 0.4488 gram CO_2 and 0.1610 gram H_2O.

II. 0.1975 gram substance gave 0.4998 gram CO_2 and 0.1815 gram H_2O.

	Calculated for $C_8H_{13}CO_2H$.	Found. I.	Found. II.
C	69.23	68.45	69.02
H	10.25	10.00	10.21

Dihydro-α-campholytic acid boils at 245° to 247°. The relation in the boiling-points of the other related acids is of special interest:

α-Campholytic acid boils at 240° to 243°.

Dihydro-α-campholytic acid boils at 245° to 247°.

β-Campholytic acid boils at 255° to 256°.

Dihydro-*β*-campholytic acid boils at 244°.

It will be seen that the addition of hydrogen to the α-acid raises its boiling-point. It seems possible that this unusual effect is connected with the peculiar structure of the acid.

The *amide* of dihydro-*i*-α-campholytic acid crystallizes in needles, which melt at 103° to 104°. Both amide and acid are stable toward permanganate.

The *α-Bromdihydro-i-α-campholytic acid*, $C_8H_{14}\begin{matrix}CO_2H\\Br\end{matrix}$, was prepared by treating the acid with phosphorus pentachloride and warming the resulting chloride with the calculated amount of bromine in a sealed tube. The phosphorus oxychloride was decomposed with ice-water, the chloride of the brom acid was then decomposed by warming with glacial formic acid, and the resulting brom acid was crystallized from formic acid. It crystallizes in needles which melt at 148°. It is difficultly soluble in cold formic acid.

0.1113 gram acid gave 0.0898 gram AgBr.

	Calculated for $C_8H_{13}O_2Br$.	Found.
Br	34.04	34.33

Δ⁵-Campholytic Acid, $C_8H_{13}CO_2H$.—The remainder of the

brom acid was treated with alcoholic potash and the acid which was formed was crystallized from ligroin, in which it is easily soluble. The new acid crystallizes in needles which melt at 90° to 91°. Curiously enough, this is almost exactly the melting-point of the tetrahydro neighboring xylic acid.[1] A mixture of the two acids, however, melts below 60°. The acid, in a sodium carbonate solution, decolorizes potassium permanganate instantly, proving that it does not contain a trimethylene grouping. The amide of Forster's infracampholenic acid also decolorizes permanganate and so can contain no trimethylene ring. The position of the double union must be Δ^5 for either Bredt's or Bouveault's formula for camphoric acid, as has been pointed out above.

The *Amide* of Δ^5-campholytic acid crystallizes from ligroin in leaflets or small plates which melt at 90°. This is also the melting-point of the amide of infracampholenic acid, but a mixture of the two melts below 75°. The two acids are, therefore, different.

On warming with dilute sulphuric acid Δ^5-campholytic acid is not converted into β-campholytic acid. In this respect it differs from both α-campholytic acid and infracampholenic acid.

As the dihydro-α-campholytic acid was prepared from a racemic acid, it must be inactive. The Δ^5-campholytic acid must also be inactive. An active dihydrocampholytic acid could, doubtless, be prepared from the active campholytic acid.

Only about a gram of the dihydro-acid has been prepared thus far and the Δ^5-acid was not obtained in sufficient quantity for analysis. Its method of formation and conduct leave no question as to its composition.

TERRE HAUTE, May 25, 1901.

Since writing the above, the dihydro-α-campholytic acid has been prepared in larger amount and the Δ^5-campholytic acid obtained by shaking the ester of the α-brom acid with a solution of barium hydroxide.[2] The acid was mixed with some of the α-hydroxy acid and was purified for the first analysis by

[1] This JOURNAL, **22**, 3.

[2] Shepherd and Noyes : This JOURNAL, **22**, 263.

distillation with water vapor, for the second analysis by distilling again, and for the third by neutralizing with ammonia and distilling a third time. The ammonium salt dissociates and passes over with the steam. The results show the progressive purification of the acid :

I. 0.1929 gram substance gave 0.4815 gram CO_2 and 0.1565 gram H_2O.

II. 0.1563 gram substance gave 0.3922 gram CO_2 and 0.1281 gram H_2O.

III. 0.1800 gram substance gave 0.4588 gram CO_2 and 0.1476 gram H_2O.

	Calculated for $C_9H_{14}O_3$.	Found. I.	II.	III.
C	70.13	68.10	68.49	69.46
H	9.09	9.02	9.10	9.11

The α-hydroxy acid has thus far been obtained only as an oil which would not solidify and which has not been analyzed. The oxidation of this acid to a ketone, by means of lead peroxide and sulphuric acid, promises to give positive evidence as to whether the Perkin-Bouveault or Bredt's formula for camphor is the true one.

Aschan[1] has recently furnished what he considers to be conclusive evidence in support of Bredt's formula, by proving that the camphane obtained by the reduction of two active bornyl iodides is inactive. The proof seems to be inconclusive, as it has not been shown that the borneol prepared from either of the bornyl iodides gives an active camphoric acid by oxidation. Each of Aschan's bornyl iodides was prepared from pinene, and Marsh and Stockdale[2] have shown that the borneol from pinene hydrochloride gives an inactive camphoric acid by oxidation. If the borneol from Aschan's bornyl iodide should also give an inactive camphoric acid, the inactivity of the camphane would furnish no evidence as to the structure of camphor. That the bornyl iodide was formed by the addition of hydriodic acid to an unsaturated compound, cannot be considered as proof that its activity is not dependent on the position of the iodine atom,[3] since Phillips and one of us[4] have shown that the addition of hydrobromic acid may

[1] Ann. Chem. (Liebig), **316**, 196.
[2] J. Chem. Soc., **87**, 964.
[3] See Aschan, *Loc. cit.*
[4] This JOURNAL, **24**, 391.

produce an active compound identical with that obtained by the replacement of a hydroxyl group by bromine. While the formulæ which we have given may not be true, there seems to be no escape from the conclusion that the activity of the bromdihydrocampholytic acid must depend, in part, on the asymmetric carbon atom to which the bromine is attached.

TERRE HAUTE, July 1, 1901.

REVIEWS.

DER FORMALDEHYD. Seine Darstellung und Eigenschaften seine Anwendung in der Technik und Medicin. Bearbeitet von DR. L. VANINO unter Mitwirkung von DR. E. SEITTER. Wien. Pest. Leipzig: A. Hartleben's Verlag. 1901. Pp. 96 + vi.

In Germany alone 400,000 kilograms of formic aldehyde are manufactured yearly. Of this large quantity, 200,000 kilograms are used in the preparation of aniline dyes, and the rest in the tanning and paper industries and as a disinfectant. This pamphlet gives a great deal of information about formic aldehyde, and chemists will find it interesting and valuable. Formic aldehyde is sometimes called methyl aldehyde and, according to the new nomenclature, *methanal*. The commercial product, which is a water solution containing about 40 per cent of the aldehyde, is known as *formalin*. As is well known, the fundamental reaction that makes formic aldehyde of such importance in the aniline-dye industry, is that which takes place between the aldehyde and aniline, giving diamidodiphenylmethane:

$$H.CHO + 2C_6H_5.NH_2 = CH_2\begin{matrix}C_6H_4NH_2\\C_6H_4NH_2\end{matrix} + H_2O.$$

When the product is mixed with aniline or with toluidine and the mixture oxidized, either pararosaniline or rosaniline is obtained.

A curious use of the aldehyde is in the preparation of fuming nitric acid. When the polymeric variety of the aldehyde, known as paraform, is added to nitric acid, nitrogen dioxide, NO, is evolved even in the cold. By heating gently and conducting the escaping gases into nitric acid, fuming nitric acid is obtained. Ludwig was the first one to make experiments on the use of formic aldehyde as a food preservative. He did not, however, sanction this use of it, as he held that the aldehyde would act injuriously on the human organism. This injurious action has been established by recent experiments of Bruns (Ann. di Farm, 1899, 324). The aldehyde has found extensive application in medicine; and as a disinfectant in cases of diphtheria, scarlet fever, measles, smallpox, tuberculosis, etc.